APPROXIMATE MOLECULAR ELECTRONIC STRUCTURE METHODS

By

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To my grandparents,

Carrie B and W D Owens

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APPROXIMATE MOLECULAR ELECTRONIC STRUCTURE METHODS

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Resonance integral formulas as derived by Linderberg and Seamans from the Heisenberg equation of motion for the position operator are incorporated into Intermediate Neglect of Differential Overlap (INDO) and Neglect of Diatomic Differential Overlap (NDDO) semi-empirical methods. Two-electron integrals consistent with the NDDO approximation are evaluated theoretically yielding an approximate Hamiltonian containing no pure parameters. When applied to a series of test molecules, results indicate that bond lengths and angles are comparable to those obtained with conventional methods. Singlet-singlet configuration interaction (CI) calculations yield spectra which tend to be blue-shifted 3,000–5,000 cm^{-1} relative to INDO/S.

CHAPTER I
INTRODUCTION AND BACKGROUND

Introduction

Such diverse processes as photosynthesis, oxygen transport, and DNA replication, processes of central importance to life as we know it, are fundamentally molecular in nature. Since much of our modern day understanding of atoms and molecules has come from the study of quantum mechanics, it is of great importance that we be able to study these processes within a quantum mechanical framework.

However, the computational demands associated with the application of quantum mechanical methods to molecules of more than a few atoms are considerable. Indeed, it was not long ago that *ab initio*[1] calculations on even small molecules were thought out of the question. According to Levine [1]

> in the 50's there was a general belief that meaningful *ab initio* calculation of molecular properties for all except very small molecules was out of the question. Quantum chemistry books written in this period contain such statements as, "we cannot hope ever to make satisfactory *ab initio* calculations [for organic compounds]" and "It is wise to renounce at the outset any attempt at obtaining precise

---

[1] *Ab initio* methods tend to make only those approximations which are necessary to keep the problem soluble.

> solutions of the Schröedinger equation for systems more complicated than the hydrogen molecule ion."

The advent and rapid development of the digital electronic computer and a greatly increased knowledge of the problem itself have rendered such statements inaccurate predictions of the future. Today, the principal limitation regarding the size of molecules upon which quantum mechanical calculations may be performed is the speed of the computer and its available storage capacity. Nonetheless, these limitations do exist and are such that *ab initio* calculations on rather large molecules such as chlorophyl, hemoglobin, and DNA are either prohibitively expensive or, in the latter case, still beyond the reach of current technology.

The importance of these molecules and the desire on the part of theoreticians to study them go far in motivating the need for approximate methods whereby the fundamental physics of the *ab initio* methods are essentially preserved but further approximations are invoked which greatly reduce the scale of the calculations. Semi-empirical methods then go a step further by replacing certain terms in the formulation with values obtained either directly or indirectly from experiment. It is this empirical aspect of semi-empirical methods which accounts for their relatively high level of accuracy despite their approximate nature.

The importance of semi-empirical methods is undisputed. From the topological Hückel π-electron theory to today's all-valence methods, semi-empirical treatments have greatly enhanced our insight into molecular electronic structure.

Despite the great successes of semi-empirical methods there are still some very valid criticisms leveled against them. One such criticism particularly relevant to this study is that current methods utilizing a single model are not capable of accurately reproducing a variety of properties over a broad range of molecules. Typically, a different model Hamiltonian is invoked for different properties. This is somewhat disturbing in that in nature, there is only one Hamiltonian--the exact one. One would never argue for example, that one set of physical forces is at work in determining molecular geometries and another, different, set is at work determining molecular transition energies. It follows then that if a model is a simplified, yet reasonably correct representation of reality, this single model should suffice. That it does not, leads one to believe that the model is lacking and needs improvement.

The limitations of *ab initio* methods combined with the past success and future potential of approximate methods is powerful motivation for further investigation of semi-empirical models. In this work two possibilities for an improved semi-empirical model are investigated. The first involves advancing from the INDO to NDDO integral approximation and the second is concerned with the formulation of two-center, one-electron Fock matrix elements--those terms primarily responsible for bonding in semi-empirical models. Chapters one and two provide the necessary background in quantum chemistry and semi-empirical methods, respectively. Chapter three describes an alternative formulation of the two-center, one-electron Fock matrix elements which is subsequently implemented at the INDO and NDDO levels. The results of geometry optimizations and singlet-singlet configuration interaction calculations using the new methods are presented in chapter four and conclusions are stated in chapter five.

It is our hope that this work represents a step in the direction of a single, semi-empirical Hamiltonian capable of predicting molecular geometries as well as electronic transition energies utilizing the fewest parameters possible.

Background

The Schrödinger Equation

One of the central problems of quantum chemistry is the solution of the nonrelativistic time independent, many-electron Schrödinger equation [2],

$$H\Phi = E\Phi \tag{1}$$

where H is the Hamiltonian operator for a system of nuclei and electrons, Φ is the wavefunction describing the system, and E is the energy of the system. Given a molecular coordinate system with $\mathbf{R}_A$, the position vector of nucleus A, and $\mathbf{r}_i$, the position vector of electron i, the Hamiltonian for N electrons and M nuclei can be written in Hartree atomic units as

$$\begin{aligned} H = & -\sum_{i=1}^{N}\frac{1}{2}\nabla_i^2 - \sum_{A=1}^{M}\frac{1}{2M_A}\nabla_A^2 - \sum_{i=1}^{N}\sum_{A=1}^{M}\frac{Z_A}{r_{iA}} \\ & + \sum_{i=1}^{N}\sum_{i<j}^{N}\frac{1}{r_{ij}} + \sum_{A=1}^{M}\sum_{B>A}^{M}\frac{Z_A Z_B}{R_{AB}} \end{aligned} \tag{2}$$

The first two terms are the operators for the kinetic energy of the N electrons and M nuclei, respectively. Since $r_{iA} = |\mathbf{r}_i - \mathbf{R}_A|$, the third term represents the coulombic nuclear-electronic attractions. Similarly, $r_{ij} = |\mathbf{r}_i - \mathbf{r}_j|$ and $R_{AB} = |\mathbf{R}_A - \mathbf{R}_B|$, so the fourth and fifth terms represent coulombic repulsions among the electrons and coulombic repulsions among the nuclei, respectively.

The Born-Oppenheimer Approximation

To completely describe a molecule we must describe the motions of its nuclei *and* its electrons. If we neglect the motion of translation[2], then we have still to consider a molecule's electronic, vibrational, and rotational motions, i.e. those motions which give rise to the internal energy of a molecule. Although these motions are in actuality coupled in a complex fashion, it would be a great simplification if it were possible to view these motions as independent and therefore, separately soluble problems.

Toward this end, we will invoke the physical picture of electrons moving among the nuclei so much more rapidly than the nuclei move themselves that we can consider the nuclei to be fixed relative to the electrons. This physical picture is the essence of the Born-Oppenheimer approximation [3] which allows us to effect a quasi-separation of variables so that the electronic coordinates depend parametrically rather than explicitly upon the nuclear coordinates. The form of the molecular wavefunction resulting from this approximation is

---

[2] The translation of the center of mass is separable and simply adds a constant to the total energy.

$$\Phi(\mathbf{r}_i, \mathbf{R}_n) = \Psi_{R_n}(\mathbf{r}_i)\Omega(\mathbf{R}_n) \tag{3}$$

where $\Omega(\mathbf{R}_n)$ is the wave function for the now separate motions of the nuclei and $\Psi_{\mathbf{R}_n}(\mathbf{r}_i)$ is the wavefunction describing the electrons in the field of "fixed" nuclei.

We can now consider a separate electronic problem given by

$$H_{el}\Psi_{el} = E_{el}\Psi_{el} \tag{4}$$

where

$$H_{el} = -\sum_{i=1}^{N}\frac{1}{2}\nabla_i^2 - \sum_{i=1}^{N}\sum_{A=1}^{M}\frac{Z_A}{r_{iA}} + \sum_{i=1}^{N}\sum_{i<j}^{N}\frac{1}{r_{ij}} \tag{5}$$

is the Hamiltonian for the electrons in the field of the fixed nuclei,

$$\Psi_{el} = \Psi_{\mathbf{R}_n}(\mathbf{r}_i) \tag{6}$$

is the electronic wavefunction and E_{el} is the electronic energy. The molecular Hamiltonian can now be rewritten as

$$H = -\sum_{A=1}^{M}\frac{1}{2M_A}\nabla_A^2 + \sum_{A=1}^{M}\sum_{A<B}^{M}\frac{Z_A Z_B}{R_{AB}} + E_{el} \tag{7}$$

which suggests that the electronic energy plus the potential energy of the nuclei form a potential within which nuclear rotations, vibrations and translations take place. The minima of this potential energy surface correspond to stable molecular geometries. In the present work we are concerned only with the electronic Hamiltonian and therefore from this point on we shall drop the "*el*" subscripts and understand that the electronic problem is implied.

Even with the considerable help afforded by the Born-Oppenheimer approximation, the electronic Schrödinger equation can be solved exactly only for one-electron systems. Now, if the universe were composed only of molecular species such as the H_2^+, He_2^{+3}, and H_2O^{+9} there would be little left to do. However, species such as these, for the most part, do not exist–they need their electrons to hold them together and we need some way of dealing with all these electrons.

The Independent Particle Approximation

The many-electron Schrödinger equation cannot be solved exactly but the one-electron problem is soluble. It seems reasonable then to wonder whether the many-electron problem might be solved if it were treated, in an approximate fashion, as many one-electron problems. More explicitly, what we would like to do is treat the *N*-electron problem as though it were *N* independent one-electron problems. The most obvious way of doing this, and the crudest approximation, is to simply ignore electron-electron interactions.

Within such an *independent particle approximation* the total Hamiltonian for the system is just the sum of the one-electron Hamiltonians. Thus, the electronic Hamiltonian becomes

$$H = h_1 + h_2 + \cdots + h_N \tag{8}$$

with

$$h_i = -\nabla_i^2 + \sum_A \frac{Z_A}{r_{iA}} \tag{9}$$

The wavefunction corresponding to a Hamiltonian of this form is a simple product of one-electron functions and the total energy is just the sum of the individual orbital eigenvalues,

$$\Psi = \chi_1(\mathbf{r}_1)\chi_2(\mathbf{r}_2) \cdots \chi_N(\mathbf{r}_N) \tag{10}$$

$$E = \epsilon_1 + \epsilon_2 + \cdots + \epsilon_N \tag{11}$$

where it is assumed that the χ_i are hydrogen-like wavefunctions or some approximation thereof.

Electron Repulsions

It is now possible to make a correction (to the energy) for electron-electron repulsions by assuming the independent particle wavefunction is correct and using it to calculate the expectation value of a Hamiltonian which includes these repulsions. Thus Hamiltonian has the form

$$H = \sum_{i} h_i + \sum_{i<j} \frac{1}{r_{ij}} \tag{12}$$

and gives rise to energy corrections of the form

$$\int \chi_i^*(i)\varphi_j^*(j)\frac{1}{r_{ij}}\chi_i(i)\chi_j(j)d\tau_i d\tau_j \tag{13}$$

which represent the mutual repulsion of the two charge distributions $|\chi_i(i)|^2$ and $|\chi_j(j)|^2$. While this in some measure corrects the energy and can provide a qualitative assessment of the effect of electron-electron repulsions, the wave function is still a poor representation of reality and gives poor quantitative results–especially as the number of electrons increases.

The Method of Hartree

In 1928 Hartree proposed the method of the self-consistent field (SCF) [4]. This method assumes that the potential experienced by a particular electron is a spherically symmetric average of the potential due to the *N-1* other electrons so that the exact two-electron potential of Eq. **(12)** is replaced by an effective potential given by

$$V = \sum_{i} V_i^{eff} = \sum_{i} \sum_{j \neq i} J_j(i) \,, \tag{14}$$

where the *Coulomb operator* has been defined as

$$J_j(i) = \int \frac{\chi_j^*(j)\chi_j(j)}{r_{ij}} d\tau_j \tag{15}$$

which, when operating on another charge distribution represents the classical interaction of two charge distributions. It is now possible to express the total N-electron Hamiltonian as a sum of *effective* one-electron Hamiltonians of the form

$$H_i^{\text{eff}} = h_i + V_i^{\text{eff}} \tag{16}$$

leading to a set of pseudo-eigenvalue equations which determine the one-electron wavefunction

$$(h_i + V_i^{\text{eff}})\varphi_i(1) = \varepsilon_i\varphi_i(1) \tag{17}$$

The difficulty with these equations is clear from Eq. (14), the effective potential for the i-th electron depends on the as yet unspecified *N-1* wavefunctions describing the remaining electrons. Hartree overcame this problem by employing a series of successive approximations. He began by assuming a set of wavefunctions (orbitals) which he hoped were reasonably accurate and proceeded to calculate the Hartree operator for the i-th electron by evaluating the integrals of the effective potential. The resulting N equations are solved for N new orbitals which are then used to compute the Hartree operator for the next iteration. The process is then repeated until the Hartree operator of the i+1 iteration is within a given tolerance of the i-th iteration at which time the potential is termed self-consistent. The resulting orbitals are then used to form a Hartree product wavefunction for the many-electron system As will be shown in the next section, Hartree's method failed primarily due to the form of the resulting product wavefunction which ignored the physical requirement of antisymmetry.

Spin and The Pauli Principle

The concept of an intrinsic angular momentum or "spin" as a fundamental property of electrons was proposed in 1925 by Uhlenbeck and Goudsmit [5,6] to account for the fine structure of atomic spectra–the doublet sodium *D* line to cite one well known example Based on the results of the Stern and Gerlach experiment [7,8], as well as spectral evidence, it was further postulated that the magnitude of this spin is $\frac{1}{2}$ unit leading to eigenvalues for s_z of $\pm\frac{1}{2}$ Thus, electronic wavefunctions should depend not only on the three spatial coordinates but on a fourth spin coordinate as well It is customary to designate this spin coordinate ω and to introduce two orthogonal functions $\alpha(\omega)$ and $\beta(\omega)$ such that

$$\langle\alpha|\alpha\rangle = \langle\beta|\beta\rangle = 1 \tag{18a}$$

$$\langle\alpha|\beta\rangle = \langle\beta|\alpha\rangle = 0 \tag{18b}$$

$$s^2|\alpha\rangle = s(s+1)|\alpha\rangle = \frac{3}{4}|\alpha\rangle \tag{19a}$$

$$s^2|\beta\rangle = s(s+1)|\beta\rangle = \frac{3}{4}|\beta\rangle \tag{19b}$$

$$s_z|\alpha\rangle = \frac{1}{2}|\alpha\rangle \tag{20a}$$

$$s_z|\beta\rangle = -\frac{1}{2}|\beta\rangle \tag{20b}$$

It is a fundamental principle of quantum mechanics that the measurement of any physical property which depends on the coordinates of a system of identical particles should not depend in any way on the arbitrary labeling of the particles. For two electrons described by $\Psi(\chi_i(1)\chi_j(2))$, there exists a probability density given by $|\Psi(\chi_i(1)\chi_j(2))|^2$ which must not depend upon the permutation of the two electronic coordinates. Thus,

$$|\Psi(\chi_i(1)\chi_j(2))|^2 = |\Psi(\chi_j(1)\chi_i(2))|^2 \tag{21}$$

leading to the possibility that

$$\Psi(\chi_i(1)\chi_j(2)) = \Psi(\chi_j(1)\chi_i(2)) \tag{22}$$

(the symmetric case), or

$$\Psi(\chi_i(1)\chi_j(2)) = -\Psi(\chi_j(1)\chi_i(2)) \tag{23}$$

(the antisymmetric case). Experimental evidence indicates that "there is no place for the symmetric solution in ordinary spectrum theory" [9] and it is a further postulate of quantum mechanics that electrons are described by antisymmetric wavefunctions The well known Pauli Exclusion Principle is a consequence of this antisymmetry requirement, for if an electron is assigned the same set of space and spin coordinates, the wavefunction, and thus the probability, vanishes in accordance with Eqs (24)

$$\Psi[x_i(1)x_j(2)] = -\Psi[x_j(1)x_i(2)] \tag{24a}$$

$$\Psi[x_i(1)x_i(2)] = 0 \tag{24b}$$

Slater Determinants

Considering the preceding discussion it is apparent that the wavefunction assumed by Hartree for the SCF procedure is incorrect. This was pointed out by Slater [10] who suggested that the assumed SCF wavefunction should be an antisymmetrized projection of Hartree products defined by

$$\psi^{HF} = \mathcal{A}\psi \tag{25}$$

where $\mathcal{A}$ is the antisymmetrizer,

$$\mathcal{A} = \frac{1}{\sqrt{N!}} \sum_{\mathcal{P}} (-1)^p \mathcal{P} \tag{26}$$

and the summation of Eq (26) is over the $N!$ possible permutations of the N particles. The exponent p, the parity of the permutation, is the number of simple two-particle interchanges required to bring a particular permutation back into its proper or normal order and the operator $\mathcal{A}$ is the antisymmetrizer. Such wavefunctions are known as *Slater determinants* and they explicitly account for the indistinguishability of the identical electrons since the permutations distribute them among all the occupied orbitals resulting from the SCF calculation.

The rows of a Slater determinant are labeled by electron coordinates (space and spin) and the columns by spin orbital labels. We see then that the interchange of any two rows of the determinant (corresponding to the interchange of electronic coordinates) reverses the sign of the determinant. Furthermore, should any two rows of the determinant be identical (corresponding to two electrons with the same space and spin coordinates), the determinant vanishes–a manifestation of the Pauli exclusion principle.

The Hartree-Fock Equations

Working independently, Fock [11] and Slater [12] put Hartree's intuitive method of the self-consistent field on a more rigorous footing by making use of the variation principle. The *variation principle* assures us that the energy obtained from an approximate wavefunction represents an upper bound to the exact ground state energy. Hence the energy becomes one measure of the quality of a wavefunction–the lower the energy the better the wavefunction. Therefore, by minimizing the energy of a Hartree product by varying the radial functions, it is possible to arrive at precisely the equations of Hartree's method. Furthermore, since it is desirable to maintain the orthonormality of the starting orbitals, the minimization is constrained by this requirement. Such a constrained minimization can be carried out using Lagrange's method of undetermined multipliers

When this same procedure is carried out using a Slater determinant rather than a Hartree product as the approximation to the ground state wavefunction, the famous Hartree-Fock equations are obtained These are given by

$$f(1)\chi_a(1) = \sum_{b=1}^{N} \varepsilon_{ba}\chi_b(1) \tag{27}$$

where f is the Fock operator, defined as

$$f(1)\chi_a(1) = \left[h(1) + \sum_{b=1}^{N} (J_b(1) - K_b(1))\right]\chi_a(1) \tag{28}$$

J being the familiar coulomb operator of the Hartree method while K is termed the exchange operator and gets its name from the exchange of electronic coordinates which takes place during its operation The exchange terms in the Hartree-Fock equations arise solely as a consequence of the antisymmetric nature of the many electron wavefunction and so did not arise in Hartree's treatment. The Coulomb and exchange integrals are defined according to Eq (29) below

$$J_b(1)\chi_a(1) = \int d\tau_2 \chi_b^*(2)\frac{1}{r_{12}}\chi_b(2)\chi_a(1) \tag{29a}$$

$$K_b(1)\chi_a(1) = \int d\tau_2 \chi_b^*(2)\frac{1}{r_{12}}\chi_b(1)\chi_a(2) \tag{29b}$$

Equation (27) can be brought into the form of a standard eigenvalue problem by means of a unitary transformation which diagonalizes the matrix of Lagrangian multipliers yielding

$$f(1)\chi_a(1) = \varepsilon_a \chi_a(1) \tag{30}$$

The electronic energy within the Hartree-Fock method is given by

$$E = \langle \Psi_0 | H | \Psi_0 \rangle = \sum_i^N \langle i|h|i\rangle + \sum_i^N \sum_{j<i}^N \langle ij|ij\rangle - \langle ij|ji\rangle \tag{31}$$

where $|\Psi_0\rangle$ is the Slater determinant formed from the N occupied Hartree-Fock orbitals and represents the best variational approximation of the ground state wavefunction using a single-determinant representation.

Molecular Orbital Theory

Historically, the Hartree Fock method described in the previous section was applied to atoms and the resulting differential equations were solved numerically and yielded highly accurate (in many cases) atomic energies and wavefunctions. Such a procedure for molecules, however, was impractical for all but diatomic molecules. Furthermore, numerical wavefunctions do not provide a convenient basis for molecular property calculations and other post-Hartree-Fock procedures.

The difficult part of the Hartree-Fock procedure is the calculation of the molecular orbitals. Addressing this question, Roothaan [13] and Hall [14] suggested that the molecular orbitals be expanded as a linear combination of some known set of basis functions according to

$$\psi_i = \sum_{\nu} \phi_\nu c_{\nu i} \tag{32}$$

where ϕ_ν is a fixed "atomic" orbital basis function and $c_{\nu i}$ is the expansion coefficient for the ν-th atomic orbital in the i-th molecular orbital. Such an expansion reduces the problem of calculating molecular orbitals from that of solving the Hartree-Fock equation numerically, to that of solving a system of linear equations algebraically for the expansion coefficients $c_{\nu i}$. Additionally, the Roothaan Hall procedure provides a definite analytic form for the molecular orbitals which can be conveniently used for the calculation of expectation values. The use of linear expansions in terms of atomic orbitals in the Hartree-Fock self-consistent field method constitutes Molecular Orbital–Linear Combination of Atomic Orbital (MO–LCAO) Theory. Since its introduction, it has been, and continues to be, one of the most pervasive and powerful tools for gaining insight into molecular electronic structure.

If we now substitute the expansion of Eq. (32) into Eq. (30) we get

$$\sum_{\nu} f\phi_\nu c_{\nu i} = \sum_{\nu} \phi_\nu c_{\nu i} \epsilon_i \tag{33}$$

Multiplication on the left of Eq. (33) by ϕ_μ, followed by integration over the electronic coordinates yields

$$\sum_{\nu} F_{\mu\nu} c_{\nu i} = \sum_{\nu} S_{\mu\nu} c_{\nu i} \epsilon_i \tag{34}$$

where F and S are the square, Hermitian matrices defined according to the basis set as

$$F_{\mu\nu} = \int \phi_\mu(1) f(1) \phi_\nu(1) d\tau_1 \tag{35}$$

and

$$S_{\mu\nu} = \int \phi_\mu(1) \phi_\nu(1) d\tau_1 \tag{36}$$

If there are N basis functions there will be N molecular orbitals and N equations of the form of Eq. (34), all of which are expressed in the single matrix equation

$$\mathbf{FC} = \mathbf{SCE} \tag{37}$$

which is the well known Roothaan Hall equation

The overlap matrix in the Roothaan equation arises from the use of a non-orthogonal basis set. However, a new coefficient matrix can be defined according to Löwdin's symmetric orthogonalization procedure [15] as

$$\mathbf{C}' = \mathbf{S}^{\frac{1}{2}}\mathbf{C} \tag{38}$$

which in turn gives

$$\mathbf{C} = \mathbf{S}^{-\frac{1}{2}}\mathbf{C}' \tag{39}$$

Using the above substitution for $\mathbf{C}$ in Eq. (37) and multiplying on the left by $\mathbf{S}^{-\frac{1}{2}}$ yields

$$\mathbf{S}^{-\frac{1}{2}}\mathbf{F}\mathbf{S}^{-\frac{1}{2}}\mathbf{C}' = \mathbf{S}^{-\frac{1}{2}}\mathbf{S}\mathbf{S}^{-\frac{1}{2}}\mathbf{C}'\mathbf{E} \tag{40}$$

Equation (40) defines the new matrix $\mathbf{F}'$ and effects a symmetric orthogonalization of the basis which results in the standard matrix eigenvalue problem

$$\mathbf{F}'\mathbf{C}' = \mathbf{E}\mathbf{C}' \tag{41}$$

or

$$(\mathbf{F}' - \mathbf{E})\mathbf{C}' = 0 \tag{42}$$

Thus equation has a nontrivial ($\mathbf{C}' \neq 0$) solution only when the determinant of $\mathbf{F}' - \mathbf{E}$ vanishes which leads to the so-called *secular equation*,[3]

$$\left|\mathbf{F}' - \mathbf{E}\right| = 0 \tag{43}$$

The determinant in the secular equation is a polynomial of degree N and therefore has N roots which are the eigenvalues of Eq. (42). Diagonalizing $\mathbf{F}'$ simultaneously gives its eigenvalues and the LCAO coefficients (since $\mathbf{C}'^{\dagger}\mathbf{F}'\mathbf{C}'$ diagonalizes F) which can then be back-transformed into the expansion coefficients of $\mathbf{F}$ according to Eq. (39).

Restricted Closed-Shell Hartree Fock Theory

Since the discussion of spin and the Pauli Principle, χ, has referred to a generalized molecular (or atomic) spin orbital–a function of the three spatial coordinates and one spin coordinate necessary to describe an electron. It is useful to introduce a set of *restricted* spin orbitals, such that two electrons may occupy the same spatial function as long as each has a different spin coordinate. These spin orbitals have the form

---

[3] The secular equation gets its name from a problem in celestial mechanics which gives rise to a determinantal equation analogous to Eq. (43).

$$\chi_i(x) = \left\{ \begin{array}{l} \psi_j(r)\,\omega(\alpha) \\ \psi_j(r)\,\omega(\beta) \end{array} \right\} \tag{44}$$

and a single determinant wavefunction formed from this set of spin orbitals such that every spatial orbital is doubly occupied--i.e., there are N electrons (N is even) $N/2$ of which have α spin and $N/2$ of which have β spin--is termed a *closed shell* wavefunction.

The Fock operator for a closed-shell system is obtained by integrating over the spin coordinates which yields

$$f(1) = h(1) + \sum_{a}^{N/2} [2J_a(1) - K_a(1)] \tag{45}$$

where

$$J_a(1) = \int dr_2 \psi_a^*(2) \frac{1}{r_{12}} \psi_a(2) \tag{46}$$

and

$$K_a(1)\psi_b(1) = \left[\int dr_2 \psi_a^*(2) \frac{1}{r_{12}} \psi_b(2) \right] \psi_a(1) \tag{47}$$

The factor of two in Eq. (45) arises since an electron in say the b-th molecular orbital will give rise to a coulomb interaction with each of the two electrons in the a-th molecular orbital and the single exchange interaction reflects the fact that there is only exchange between electrons of like spin. The energy of a restricted closed-shell determinant is

$$
\begin{aligned}
E &= 2\sum_{a}(a|h|a) + \sum_{a\,b}[2(ab|ab) - (ab|ba)] \\
&= 2\sum_{a} h_{aa} + \sum_{a,b}[2J_{ab} - K_{ab}]
\end{aligned}
\tag{48}
$$

and the energy of an electron in the i-th orbital is

$$
\varepsilon_i = h_{ii} + \sum_{a}[2J_{ia} - K_{ia}] \tag{49}
$$

The restricted open-shell [16] and unrestricted [17] Hartree-Fock methods will not be discussed in detail here. This is not to downplay the importance and utility of these methods. However, the closed-shell case demonstrates the essential features of the theory and provides a less complex framework for the discussion of approximate semi-empirical Hamiltonians. No loss in generality results.

The Closed-Shell Expression for the Fock Operator

We are now in a position to derive an expression for the matrix elements of the closed-shell Fock operator. These matrix elements are given by

$$
\langle\mu|f|\nu\rangle = \langle\mu|h|\nu\rangle + \sum_{a}^{N/2}[2\langle\mu|J_a|\nu\rangle - \langle\mu|K_a|\nu\rangle] \tag{50}
$$

where elements of the Coulomb matrix for a-th molecular orbital are

$$
\langle\mu|J_a|\nu\rangle = \langle\mu|\int dr_2\psi_a^{*}\frac{1}{r_{12}}\psi_a|\nu\rangle = (\mu\nu|aa) \tag{51}
$$

and

$$\langle\mu|K_a|\nu\rangle = \langle\mu a|a\nu\rangle \tag{52}$$

for the exchange operator. Combining Eq. (50), Eq. (51), and Eq. (52) gives the mixed molecular orbital-atomic orbital integral expression

$$f_{\mu\nu} = h_{\mu\nu} + \sum_{a}^{N/2} [2\langle\mu a|\nu a\rangle - \langle\mu a|a\nu\rangle] \tag{53}$$

Inserting the linear expansion of Eq. (32) for the a-th MO yields

$$\begin{aligned} f_{\mu\nu} &= h_{\mu\nu} + \sum_{a}^{N/2}\sum_{\sigma\lambda} C_{\lambda a}C_{\sigma a}^{*}[2\langle\mu\sigma|\nu\lambda\rangle - \langle\mu\sigma|\lambda\nu\rangle] \\ &= h_{\mu\nu} + 2\sum_{a}^{N/2}\sum_{\sigma\lambda} C_{\lambda a}C_{\sigma a}^{*}\left[\langle\mu\sigma|\nu\lambda\rangle - \frac{1}{2}\langle\mu\sigma|\lambda\nu\rangle\right] \\ &= h_{\mu\nu} + G_{\mu\nu} \end{aligned} \tag{54}$$

The two-electron contributions, $G_{\mu\nu}$, are further refined according to

$$\begin{aligned} G_{\mu\nu} &= 2\sum_{a}^{N/2}\sum_{\sigma\lambda} C_{\lambda a}C_{\sigma a}^{*}\left[\langle\mu\sigma|\nu\lambda\rangle - \frac{1}{2}\langle\mu\sigma|\lambda\nu\rangle\right] \\ &= \sum_{\sigma\lambda} 2\sum_{a}^{N/2} C_{\lambda a}C_{\sigma a}^{*}\left[\langle\mu\sigma|\nu\lambda\rangle - \frac{1}{2}\langle\mu\sigma|\lambda\nu\rangle\right] \\ &= \sum_{\sigma\lambda} P_{\lambda\sigma}\left[\langle\mu\sigma|\nu\lambda\rangle - \frac{1}{2}\langle\mu\sigma|\lambda\nu\rangle\right] \end{aligned} \tag{55}$$

where $P_{\lambda\sigma}$ are the Fock-Dirac or first order density matrix elements which for an orthogonal set of basis functions correspond to the charge (one-center elements) and bond order (two-center elements) matrix elements defined as

$$P_{\lambda\sigma} = 2\sum_{a}^{N/2} C_{\lambda a}C_{\sigma a}^{*} \tag{56}$$

Thus, the final expression for the elements of the Fock matrix is

$$F_{\mu\nu} = h_{\mu\nu} + \sum_{\sigma\lambda} P_{\lambda\sigma}\left[(\mu\sigma|\nu\lambda) - \frac{1}{2}(\mu\sigma|\lambda\nu)\right] \tag{57}$$

It is the evaluation and manipulation of the two-electron integrals contributing to the Fock matrix which constitute the major difficulty in carrying out MO LCAO SCF calculations The number of these integrals (neglecting symmetry) is given by

$$\frac{N}{4}(N+1)\left[\frac{N}{2}(N+1)+1\right] \approx \frac{N^4}{8} \tag{58}$$

Thus a valence-only minimal basis set calculation on water (6 basis functions) involves 231 two-electron integrals For a similar calculation on formaldehyde (10 basis functions), the number is 1,540 and for benzene (30 basis functions), the number escalates to 108,345

Since the formation of the Fock matrix (an N^4 procedure) and the manipulation of the two-electron integrals is such a formidable task in molecular calculations, quantum chemists have long sought approximations to the full Hartree-Fock equations which reduce their scale while still providing accurate results within a physically meaningful model These approximations generally seek to reduce the number of two-electron integrals by neglecting a majority of them in some systematic way When the neglect of some two-electron integrals is combined with a replacement of other one- and two-electron integrals by values taken from experiment, the resulting procedure is referred to as a semi-empirical method.

Since almost all approximate methods, including those to be developed in this work, are semi-empirical in nature we shall turn our attention to a discussion of several of these in the next chapter.

CHAPTER 2
SEMI-EMPIRICAL METHODS

Introduction

Motivation

The need for semi-empirical methods can be discussed in terms of the three areas in which it enhances the science of quantum chemistry. These are 1) the ability to perform routine calculations more quickly; 2) the ability to perform state-of-the-art calculations on systems too large to be attempted with *ab initio* methods, and 3) the ability to fine tune a semi-empirical method to the point that it can predict experimental results more accurately than a strictly *ab initio* method.

Even though computers are growing ever faster and computing time is becoming correspondingly less expensive, it cannot be said that the need for semi-empirical methods is just as rapidly diminishing. It is important that quantum mechanical methods should be routinely available not only to the theoretical researcher but also to the industrial chemist and the college sophomore. For this to be possible, the methods must be relatively small-scale and inexpensive. It is semi-empirical methods which, to an appreciable degree, meet this criterion. For they reduce many interesting and practical applications to a scale that can be performed with the computer facilities typically available to the bench chemist or the graduate student.

A recent study of the reaction center of photosynthetic bacteria [18] included semi-empirical spectroscopic calculations (singlet-singlet CI) which reproduced the lowest excitation to within approximately 300 cm^{-1} of the experimentally observed value. This calculation involved 518 atoms and about 1,400 (valence-only) basis functions. It is instructive to indulge briefly in a very approximate numbers game which should provide an estimate of the scale of such a calculation via *ab initio* methods.

Assuming 10 basis functions per atom or 5,180 basis functions implies 87,249,408,020,000, or roughly 87 trillion, two-electron integrals. Storing these integrals on disk as IEEE double precision floating point numbers will require 8 bytes for each integral plus an additional 16 bytes for each set of labels (4 bytes times 4 labels) for a total of 24 bytes per integral or 2,094 trillion bytes of disk storage. Now, using 1.2 Gbyte magnetic storage disks which are becoming common in scientific computing centers, we will require about 17.5 million disk drives to accommodate the two-electron integrals alone. If we next assume that we have a very fast computer capable of say, 100 MFLOPS (Million Floating-point Operations Per Second) and that the integrals can be pipelined very efficiently through the floating-point processor, i.e. so that there are no memory or disk access delays, then the SCF itself should take approximately 700 million seconds or about 22 years per cycle. Assuming we are still interested in the problem, we must now transform the integrals in preparation for a CI calculation--an N^5 procedure at best. This will take about 1.1 million years.

At this point we might begin to think about the size of the CI matrix but I think the point is clear--if we are going to apply quantum mechanical methods to systems such as the photosynthetic center mentioned above, semi-empirical methods are the only means possible given the current level of technology.

Finally, the accuracy with which a particular method or model predicts observations is not to be overlooked. For example assuming the very large *ab initio* calculation of the above example could be carried out, evidence indicates that the result would not be very accurate. This points to another strong argument for the use of semi-empirical methods. The ability to parameterize an approximate method on experiment can lead to very accurate results for a specific physical observable. Of course it is true that such a method, parameterized to predict accurately, say, the spectra of third row transition metals, may not do a very good job in other areas. Nonetheless, the accuracy attained by some semi-empirical models makes them very useful, albeit specific, tools in the study of molecular structure.

Rotational Invariance

Whatever else we ask of a theoretical model, we want first and foremost for it to provide us with physically meaningful results. For it to do otherwise is at best unsatisfying and at worst, could lead to scientific disaster (or at least embarrassment). And, this in fact was one of the obstacles to success in the early development of valence-only semi-empirical models. Simple attempts to extend PPP-like theories to all valence basis sets were unsuccessful since they ignored the physical requirement of rotational invariance.

It was Pople [19] and separately, Manne [20,21], who realized that the approximations and parameterizations employed in a particular model should lead to the same results for different bases related by a unitary or orthogonal transformation. The validity of this requirement can be seen by considering the non-hybridized atomic orbital bases $\varphi^{\dagger}$ and $\varphi'^{\dagger}$ related by a unitary transformation T such that $\varphi^{\dagger} = \varphi'^{\dagger}T$. In the transformed basis the Hartree Fock equations can be written in matrix form as

$$\mathbf{F}'\mathbf{C}' = \varepsilon\mathbf{S}'\mathbf{C}' \tag{59}$$

If we now multiply from the left of Eq. (59) by $\mathbf{T}$ and insert the unit matrix $\mathbf{1} = \mathbf{T}^{\dagger}\mathbf{T}$ we get

$$\mathbf{T}\mathbf{F}'\mathbf{T}^{\dagger}\mathbf{T}\mathbf{C}' = \varepsilon\mathbf{T}\mathbf{S}'\mathbf{T}^{\dagger}\mathbf{T}\mathbf{C}' \tag{60}$$

which reduces to

$$\mathbf{F}\mathbf{T}\mathbf{C}' = \varepsilon\mathbf{S}\mathbf{T}\mathbf{C}' \tag{61}$$

and implies that $\mathbf{C} = \mathbf{T}\mathbf{C}'$. Finally, the equivalence of the two resulting sets of molecular orbitals can be seen from

$$\psi^{\dagger} = \varphi^{\dagger}\mathbf{C} = \varphi^{\dagger}\mathbf{T}\mathbf{C}' = \varphi'^{\dagger}\mathbf{C}' = \psi'^{\dagger} \tag{62}$$

This invariance is assured in non-empirical methods by the invariance of the Fock operator to unitary transformations.

However, when we begin making approximations which reduce the number of integrals in the full Roothaan LCAO SCF equations, it may happen that these approximations lead to results which are not invariant to transformations which

1. Mix atomic orbitals having the same principal and azimuthal quantum numbers on the same atomic center.
2. Mix atomic orbitals of differing principal or azimuthal quantum numbers on the same atomic centers (hybrid atomic orbitals).
3. Mix atomic orbitals without regard to quantum numbers or atomic centers (symmetry adapted orbitals).

One of the characteristics common to all of the ZDO models developed by Pople and his coworkers is their invariance to the first and second types of transformations above.

The Core Hamiltonian

Another characteristic commonly found in valence only semi-empirical methods is the removal of inner shell electrons by assuming they contribute an effective electrostatic potential which screens the valence electrons from the field of nuclear charges. In the case that the screening is 100% effective we can write the valence-only core Hamiltonian operator as

$$\hat{h}_i^c = -\frac{1}{2}\nabla_i^2 - \sum_C \frac{Z'_C}{r_{iC}} \tag{63}$$

where Z'_C is the atomic valence charge of nucleus C. (Note that since e in atomic units is unity, we must explicitly include the minus sign in the equations.) Thus, the general expression for the core Hamiltonian matrix elements is

$$\begin{aligned} H^c_{\mu_A\nu_B} &= \langle\mu_A|\hat{h}_i^c|\nu_B\rangle \\ &= \langle\mu_A| -\frac{1}{2}\nabla_i^2 - \sum_C V_C|\nu_B\rangle \\ &= \langle\mu_A| -\frac{1}{2}\nabla_i^2|\nu_B\rangle - \sum_C\langle\mu_A|V_C|\nu_B\rangle \end{aligned} \tag{64}$$

where

$$V_C \equiv \frac{Z'_C}{r_{iC}} \tag{65}$$

Before considering the various ZDO methods in detail it is helpful to write down the general form of the core Hamiltonian within our assumption of an orthogonal s,p type atomic orbital basis set. As will be the case throughout this development there are three cases to be considered, namely

1. $\mu = \nu$; $A = B$ One-Center Diagonal
2. $\mu \neq \nu$; $A = B$ One-Center, Off-Diagonal
3. $\mu \neq \nu$; $A \neq B$ Two-Center

In cases one and two the core Hamiltonian can be separated into a sum of one-center and two-center parts as follows

1 $\mu = \nu, \quad A = B$

$$H^{c}_{\mu_A\mu_A} = \langle\mu_A| -\frac{1}{2}\nabla_i^2 + V_A|\mu_A\rangle - \sum_{C \neq A} \langle\mu_A|V_C|\mu_A\rangle \tag{66}$$

2. $\mu \neq \nu, \quad A = B$

$$H^{c}_{\mu_A\nu_A} = \langle\mu_A| -\frac{1}{2}\nabla_i^2 + V_A|\nu_A\rangle - \sum_{C \neq A} \langle\mu_A|V_C|\nu_A\rangle \tag{67}$$

Now, referring to the purely one-center part of H^c as U and noting that in an s,p basis the one-center, off-diagonal kinetic energy integrals vanish, as do the one-center, off-diagonal nuclear attraction integrals, leads to the result

1. $\mu = \nu, \quad A = B$

$$H^{c}_{\mu_A\mu_A} = U_{\mu_A\mu_A} - \sum_{C \neq A} \langle\mu_A|V_C|\mu_A\rangle \tag{68}$$

2. $\mu \neq \nu, \quad A = B$

$$H^{c}_{\mu_A\nu_A} = - \sum_{C \neq A} \langle\mu_A|V_C|\nu_A\rangle \tag{69}$$

3. $\mu \neq \nu$; $A \neq B$

$$B^{c}_{\mu_A\nu_B} = \langle\mu_A| -\frac{1}{2}\nabla_i^2|\nu_B\rangle - \sum_C \langle\mu_A|V_C|\nu_B\rangle \tag{70}$$

The Complete Neglect of Differential Overlap

Zero Differential Overlap

The Complete Neglect of Differential Overlap (CNDO) [19] is the most approximate of the methods to be introduced in this chapter. It is implemented by applying the zero differential overlap approximation to all products of atomic orbitals $\phi_\mu\phi_\nu$, where $\mu \neq \nu$. Thus the matrix of overlap integrals is simplified to the unit matrix. Furthermore, this approximation restricts the types of two-electron integrals which are nonzero to two; 1) one-center Coulomb integrals, and 2) two-center Coulomb integrals—all three and four-center, two-electron integrals are neglected (as is the case in all of the semi-empirical methods considered in this work). Further note that there are no exchange type integrals included at the CNDO level of approximation (this is not true of INDO, and NDDO, to be introduced in subsequent sections, which do not neglect one-center exchange integrals). These implications are summarized in Eq. (71)

$$S_{\mu_A\nu_B} = \delta_{\mu\nu} \tag{71a}$$

$$(\mu_A\lambda_C|\nu_B\sigma_D) = \delta_{\mu\nu}\delta_{\lambda\sigma}(\mu_A\lambda_C|\mu_A\lambda_C) \tag{71b}$$

If we now incorporate the simplifications that result from this first approximation into the Roothaan equations for the closed-shell case, the following expressions are obtained.

1. Case $\mu = \nu$, $A = B$

$$\begin{aligned}
F_{\mu_A\mu_A} = H_{\mu_A\mu_A} &+ \sum_{C}\sum_{\lambda_C}\sum_{D}\sum_{\sigma_D} P_{\sigma_D\lambda_C}(\mu_A\lambda_C|\mu_A\sigma_D) \\
&- \frac{1}{2}\sum_{C}\sum_{\lambda_C}\sum_{D}\sum_{\sigma_D} P_{\sigma_D\lambda_C}(\mu_A\lambda_C|\sigma_D\mu_A) \\
= H_{\mu_A\mu_A} &+ \sum_{C}\sum_{\lambda_C}\sum_{D}\sum_{\sigma_D} P_{\sigma_D\lambda_C}(\mu_A\lambda_C|\mu_A\sigma_D)\delta_{CD}\delta_{\lambda\sigma} \\
&- \frac{1}{2}\sum_{C}\sum_{\lambda_C}\sum_{D}\sum_{\sigma_D} P_{\sigma_D\lambda_C}(\mu_A\lambda_C|\sigma_D\mu_A)\delta_{AD}\delta_{AC}\delta_{\mu\sigma}\delta_{\lambda\mu} \\
= H_{\mu_A\mu_A} &+ \sum_{C}\sum_{\lambda_C} P_{\lambda_C\lambda_C}(\mu_A\lambda_C|\mu_A\lambda_C) \\
&- \frac{1}{2}\sum_{C}\sum_{\lambda_C} P_{\mu_A\mu_A}(\mu_A\mu_A|\mu_A\mu_A) \qquad (72)
\end{aligned}$$

2. Case $\mu \neq \nu$; $A = B$

$$\begin{aligned}
F_{\mu_A\nu_A} = H_{\mu_A\nu_A} &+ \sum_{C}\sum_{\lambda_C}\sum_{D}\sum_{\sigma_D} P_{\sigma_D\lambda_C}(\mu_A\lambda_C|\nu_A\sigma_D) \\
&- \frac{1}{2}\sum_{C}\sum_{\lambda_C}\sum_{D}\sum_{\sigma_D} P_{\sigma_D\lambda_C}(\mu_A\lambda_C|\sigma_D\nu_A) \\
= H_{\mu_A\nu_A} &+ \sum_{C}\sum_{\lambda_C}\sum_{D}\sum_{\sigma_D} P_{\sigma_D\lambda_C}(\mu_A\lambda_C|\nu_A\sigma_D)\delta_{CD}\delta_{\mu\nu}\delta_{\lambda\sigma} \\
&- \frac{1}{2}\sum_{C}\sum_{\lambda_C}\sum_{D}\sum_{\sigma_D} P_{\sigma_D\lambda_C}(\mu_A\lambda_C|\sigma_D\nu_A)\delta_{AD}\delta_{AC}\delta_{\mu\sigma}\delta_{\lambda\nu} \\
= H_{\mu_A\nu_A} &- \frac{1}{2}P_{\mu_A\nu_A}(\mu_A\nu_A|\mu_A\nu_A) \qquad (73)
\end{aligned}$$

3 Case $\mu \neq \nu, \quad A \neq B$:

$$\begin{aligned} F_{\mu_A\nu_B} &= H_{\mu_A\nu_B} + \sum_{C}\sum_{\lambda_C}\sum_{D}\sum_{\sigma_D} P_{\sigma_D\lambda_C}(\mu_A\lambda_C|\nu_B\sigma_D) \\ &\quad - \frac{1}{2}\sum_{C}\sum_{\lambda_C}\sum_{D}\sum_{\sigma_D} P_{\sigma_D\lambda_C}(\mu_A\lambda_C|\sigma_D\nu_B) \\ &= H_{\mu_A\nu_B} + \sum_{C}\sum_{\lambda_C}\sum_{D}\sum_{\sigma_D} P_{\sigma_D\lambda_C}[(\mu_A\lambda_C|\nu_B\sigma_D)\delta_{AB}\delta_{CD}\delta_{\mu\nu}\delta_{\lambda\sigma} \\ &\quad - \frac{1}{2}\sum_{C}\sum_{\lambda_C}\sum_{D}\sum_{\sigma_D} P_{\sigma_D\lambda_C}(\mu_A\lambda_C|\sigma_D\nu_B)\delta_{AD}\delta_{BC}\delta_{\mu\sigma}\delta_{\lambda\nu} \\ &= H_{\mu_A\nu_B} - \frac{1}{2}P_{\mu_A\nu_B}(\mu_A\nu_B|\mu_A\nu_B) \end{aligned} \tag{74}$$

Rotationally Invariant Two-Electron Integrals

There is no question that the above expressions greatly simplify the effort required to calculate the elements of the Fock matrix. However, with this simplification comes a new difficulty--namely we have introduced rotational variance into the expressions

Consider for example the integral $(s_A s_A|p_{xB} p_{xB})$ Such an integral is nonzero. However, if we now rotate the local coordinate systems of atoms A and B by, say 45° (counterclockwise), the following atomic orbital transformations occur

$$\begin{aligned} s'_A &= s_A \\ p'_{x_B} &= \frac{1}{\sqrt{2}}(p_{x_B} + p_{y_B}) \\ p'_{y_B} &= \frac{1}{\sqrt{2}}(p_{y_B} - p_{x_B}) \end{aligned} \tag{75}$$

This means that the integral $\langle s_A s_A | p_{x_B} p_{x_B} \rangle$, which is nonzero in one local coordinate system, becomes

$$\langle s_A s_A | p'_{x_B} p'_{x_B} \rangle = \frac{1}{2}[\langle s_A s_A | p_{x_B} p_{x_B} \rangle + 2\langle s_A s_A | p_{x_B} p_{y_B} \rangle + \langle s_A s_A | p_{y_B} p_{y_B} \rangle] \tag{76}$$

in the new coordinate system. Since integrals of the form

$$\langle s_A s_A | p'_{x_B} p'_{y_B} \rangle = \frac{1}{2}[\langle s_A s_A | p_{y_B} p_{y_B} \rangle - \langle s_A s_A | p_{x_B} p_{x_B} \rangle] \tag{77}$$

are to be neglected (i.e. assumed to be zero) regardless of the choice of coordinate system, it follows that

$$\langle s_A s_A | p_{y_B} p_{y_B} \rangle = \langle s_A s_A | p_{x_B} p_{x_B} \rangle \tag{78}$$

which is consistent with the result

$$\langle s_A s_A | p'_{x_B} p'_{x_B} \rangle = \frac{1}{2}[\langle s_A s_A | p_{x_B} p_{x_B} \rangle + \langle s_A s_A | p_{y_B} p_{y_B} \rangle] \tag{79}$$

and which becomes a condition that must be enforced if the CNDO method is to be rotationally invariant.

Therefore, to enforce such a condition it is assumed that the values of the two-electron integrals are independent of the specific atomic orbitals and become instead a property of the atom A or the atom pair A-C,

$$(\mu_A\lambda_A|\mu_A\lambda_A) = \gamma_{AA} \tag{80a}$$

$$(\mu_A\lambda_C|\mu_A\lambda_C) = \gamma_{AC} \tag{80b}$$

This satisfies the requirement of rotational invariance where the two-electron integrals are concerned and allows further simplification of the Fock matrix element expressions to

1. Case $\mu = \nu$; $A = B$

$$F_{\mu_A\mu_A} = H_{\mu_A\mu_A} - \frac{1}{2}P_{\mu_A\mu_A}\gamma_{AA} + \sum_{C}\sum_{\lambda_C} P_{\lambda_C\lambda_C}\gamma_{AC} \tag{81}$$

2. Case $\mu \neq \nu$, $A = B$

$$F_{\mu_A\nu_A} = H_{\mu_A\nu_A} - \frac{1}{2}P_{\mu_A\nu_A}\gamma_{AA} \tag{82}$$

3 Case $\mu \neq \nu$, $A \neq B$

$$F_{\mu_A\nu_B} = H_{\mu_A\nu_B} - \frac{1}{2}P_{\mu_A\nu_B}\gamma_{AB} \tag{83}$$

The Core Hamiltonian

Having discussed so far how the ZDO approximation is applied to two-electron integrals within the CNDO method, it is now necessary to examine the effects of the ZDO approximation upon the one-electron integrals and the subsequent consequences for the form of the core Hamiltonian. Beginning with the expression of Eq. (64) we note first that all three-center nuclear-electronic attraction integrals are neglected and of the remaining one- and two-center integrals, only those contributing to the matrix elements along the diagonal are retained according to Eq. (84),

$$\langle\mu_A|V_B|\nu_C\rangle = \langle\mu_A|V_B|\mu_A\rangle\delta_{\mu\nu} \qquad (ZDO) \qquad (84)$$

However, we have once again introduced an approximation which is not rotationally invariant by neglecting only the off-diagonal, one-center nuclear attraction integrals. This problem is corrected much as it was for the two-electron integrals. Specifically, they are assumed to be independent of the specific orbitals and become instead a characteristic of the atom pair involved. This approximation is expressed as

$$\langle\mu_A|V_B|\mu_A\rangle = \langle\overline{\mu_A}|V_B|\overline{\mu_A}\rangle \equiv V_{AB} \qquad (Rotational\ \ Invariance) \qquad (85)$$

Rewriting the Fock matrix expressions in terms of the latest assumptions and with the core Hamiltonian now written as

$$H_{\mu_A\mu_A} = U_{\mu_A\mu_A} - \sum_{C \neq A} V_{AC} \tag{86}$$

yields

1 Case $\mu = \nu$, $A = B$

$$\begin{aligned} F_{\mu_A\mu_A} &= U_{\mu_A\mu_A} - \sum_{C \neq A} V_{AC} - \frac{1}{2} P_{\mu_A\mu_A} \gamma_{AA} \\ &\quad + \sum_{C} \sum_{\lambda_C} P_{\lambda_C\lambda_C} \gamma_{AC} \\ &= U_{\mu_A\mu_A} - \frac{1}{2} P_{\mu_A\mu_A} \gamma_{AA} + \sum_{\lambda_A} P_{\lambda_A\lambda_A} \gamma_{AA} \\ &\quad + \sum_{C \neq A} [-V_{AC} + \sum_{\lambda_C} P_{\lambda_C\lambda_C} \gamma_{AC}] \end{aligned} \tag{87}$$

2 Case $\mu \neq \nu$, $A = B$

$$H_{\mu_A\nu_A} = 0 \tag{88}$$

$$F_{\mu_A\nu_A} = -\frac{1}{2} P_{\mu_A\nu_A} \gamma_{AA} \tag{89}$$

3 Case $\mu \neq \nu$; $A \neq B$ This case should really remain unchanged until the next approximation However, we should note that to remain consistent with

the development, all three-center nuclear attraction integrals are neglected.

$$H_{\mu_A\nu_B} = \langle\mu_A| -\frac{1}{2}\nabla^2 - V_A - V_B|\nu_B\rangle \tag{90}$$

$$F_{\mu_A\nu_B} = \langle\mu_A| -\frac{1}{2}\nabla^2 - V_A - V_B|\nu_B\rangle - \frac{1}{2}P_{\mu_A\nu_B}\gamma_{AB} \tag{91}$$

The Two-Center Core Elements

Finally, all two-center core Hamiltonian matrix elements are considered to be empirically determined parameters,

$$H^c_{\mu_A\nu_B} = \langle\mu_A| -\frac{1}{2}\nabla^2 - V_A - V_B|\nu_B\rangle \equiv \beta_{\mu_A\nu_B} \tag{92}$$

leaving

$$F_{\mu_A\nu_B} = \beta_{\mu_A\nu_B} - \frac{1}{2}P_{\mu_A\nu_B}\gamma_{AB} \tag{93}$$

for the two-center Fock matrix elements. The choice of values for these parameters, the so-called resonance integrals, is very important since they represent bonding interactions in a molecule.

Equation Summary

Before concluding this section, we will summarize the CNDO Fock matrix expressions. In doing so we introduce the following standard notation,

$$P_{AA} \equiv \sum_{\lambda_A} P_{\lambda_A\lambda_A} \tag{94}$$

which is incorporated into the final expressions below

CNDO Fock Matrix Element Expressions

1 Case $\mu = \nu$, $A = B$

$$F_{\mu_A\mu_A} = U_{\mu_A\mu_A} + P_{AA}\gamma_{AA} - \frac{1}{2}P_{\mu_A\mu_A}\gamma_{AA} + \sum_{C\neq A}[P_{CC}\gamma_{AC} - V_{AC}] \tag{95}$$

2 Case $\mu \neq \nu$, $A = B$

$$F_{\mu_A\nu_A} = -\frac{1}{2}P_{\mu_A\nu_A}\gamma_{AA} \tag{96}$$

3 Case $\mu \neq \nu$; $A \neq B$

$$F_{\mu_A\nu_B} = \beta_{\mu_A\nu_B} - \frac{1}{2}P_{\mu_A\nu_B}\gamma_{AB} \tag{97}$$

The Intermediate Neglect of Differential Overlap

Since the Intermediate Neglect of Differential Overlap (INDO) [22] and the CNDO methods are so closely related, it is perhaps easiest to describe INDO in terms of how it differs from CNDO This difference is found in the treatment of the one center, two-electron integrals Whereas CNDO neglects all such integrals which violate the ZDO approximation, INDO is somewhat more selective–retaining all one-center, two-electron integrals The two-center, two-electron integrals are treated as in the CNDO method, retaining only those representing Coulombic interactions and setting their value to a rotationally invariant parameter, γ_{AB}

While it is clear that the INDO method includes more two-electron integrals and is therefore less approximate than the CNDO method, it is important to understand how keeping these terms enhances our approximate description of electronic structure For a brief illustration consider the ^3P, ^1D, and ^1S terms of the $(1s)^2(2s)^2(2p)^2$ configuration of the carbon atom These terms differ from each other in energy due to the exchange integrals of the form

$$(p_x p_y | p_y p_x) \tag{98}$$

Such integrals are neglected within the CNDO approximation thereby causing the various terms to be degenerate The INDO method retains such integrals and is capable of resolving these terms into their different energy levels and providing a more accurate electronic description of the carbon atom

To arrive at the appropriate Fock matrix expressions we simply proceed as in the CNDO approximation adding the missing one-center, two-electron integrals to the one-center elements of the Fock matrix The resulting expressions are summarized below

INDO Fock Matrix Element Expressions

1. Case $\mu = \nu$, $A = B$

$$F_{\mu_A\mu_A} = U_{\mu_A\mu_A} + \sum_{C \neq A} [P_{CC}\gamma_{AC} - V_{AC}] + \sum_{\lambda_A}\sum_{\sigma_A} P_{\sigma_A\lambda_A}\left[(\mu_A\lambda_A|\mu_A\sigma_A) - \frac{1}{2}(\mu_A\lambda_A|\sigma_A\mu_A)\right] \tag{99}$$

2. Case $\mu \neq \nu$, $A = B$

$$F_{\mu_A\nu_A} = \sum_{\lambda_A}\sum_{\sigma_A} P_{\sigma_A\lambda_A}\left[(\mu_A\lambda_A|\nu_A\sigma_A) - \frac{1}{2}(\mu_A\lambda_A|\sigma_A\nu_A)\right] \tag{100}$$

3. Case $\mu \neq \nu$, $A \neq B$

$$F_{\mu_A\nu_B} = \beta_{\mu_A\nu_B} - \frac{1}{2}P_{\mu_A\nu_B}\gamma_{AB} \tag{101}$$

The Neglect of Diatomic Differential Overlap

The Neglect of Diatomic Differential Overlap [19] (NDDO) is the least approximate of the methods discussed and is also the easiest to describe. Just as in the CNDO and INDO methods, the ZDO approximation is applied to the overlap yielding a unit overlap matrix,

$$S_{\mu_A\nu_B} = \delta_{\mu\nu} \tag{102}$$

As for the two-electron integrals, the ZDO approximation is invoked such that the differential overlap of orbitals on different centers is zero so that the general integral is

$$\langle \mu_A \lambda_C | \nu_B \sigma_D \rangle = \langle \mu_A \lambda_C | \nu_A \sigma_C \rangle \delta_{AB} \delta_{CD} \tag{103}$$

So once again all three and four-center integrals are neglected. As in INDO all one-center integrals are kept as are all two-center Coulombic integrals. Unlike INDO, NDDO retains two-center, dipole-dipole interactions of the form

$$\langle \mu_A \sigma_B | \nu_A \lambda_B \rangle \qquad \{\mu \neq \nu; \sigma \neq \lambda\} \tag{104}$$

These integrals are known to be important for a proper representation of lone pair repulsions in molecules such as hydrazine and hydrogen peroxide

Another major distinction between NDDO and INDO (or CNDO) is found in the core Hamiltonian matrix elements. Since we are no longer neglecting monatomic differential overlap the approximation of Eq. (84) is no longer valid and all two-center nuclear-electronic attraction integrals must be retained. The expression for the one-center core Hamiltonian becomes

$$H^c_{\mu_A \nu_A} = U_{\mu_A \nu_A} - \sum_{C \neq A} \langle \mu_A | V_C | \nu_A \rangle \tag{105}$$

However, the two-center core Hamiltonian matrix elements $H^c_{\mu_A \nu_B}$ $(A \neq B)$ include three-center nuclear-electronic attraction integrals of the form $\langle \mu_A | V_C | \nu_B \rangle$

which consequently are neglected (since it would be inconsistent to keep these as the only three-center terms) leaving

$$H^{c}_{\mu_A\nu_B} = \left\langle \mu_A \right| -\frac{1}{2}\nabla^2 - V_A - V_B \left| \nu_B \right\rangle \tag{106}$$

As for CNDO and INDO these terms are usually treated as pure parameters in accordance with Eq. (92).

It is worth noting at this point that the largest three-center terms entering the Fock matrix element $F_{\mu\nu}$ are of the form

$$-\sum_{C} \langle \mu_A | V_C | \nu_B \rangle + \sum_{C} \sum_{\lambda_C} P_{\lambda_C \lambda_C} (\mu_A \lambda_C | \nu_B \lambda_C) \tag{107}$$

If we now approximate the two-electron integrals according to (see Eq. (169), pg. 73)

$$(\mu_A \lambda_c | \nu_B \lambda_C) \approx (\mu_A \overline{\lambda_C} | \nu_B \overline{\lambda_C}) \equiv (\mu_A s_C | \nu_B s_C) \tag{108}$$

and the nuclear-electronic attraction integrals as

$$\langle \mu_A | V_C | \nu_B \rangle \approx Z'_C (\mu_A s_C | \nu_B s_C) \tag{109}$$

then Eq. (107) can be written

$$-\sum_{C} (Z'_C - P_{CC}) (\mu_A s_C | \nu_B s_C) \tag{110}$$

This suggests that the three-center terms might tend to cancel in all but the most polar molecules in which cases these terms probably represent the largest source of errors in the NDDO method

The expressions for the elements of the Fock matrix are relatively easily obtained from the full expressions The details can be found in appendix B and the results are summarized below

NDDO Fock Matrix Element Expressions

1 Case $\mu = \nu,\quad A = B$

$$\begin{aligned} F_{\mu_A\mu_A} &= U_{\mu_A\mu_A} \\ &+ \sum_{C\neq A}\sum_{\lambda_C}\sum_{\sigma_C} P_{\sigma_C\lambda_C}\left[(\mu_A\lambda_C|\mu_A\sigma_C) - (\mu_A|V_C|\mu_A)\right] \\ &+ \sum_{\lambda_A}\sum_{\sigma_A} P_{\sigma_A\lambda_A}\left[(\mu_A\lambda_A|\mu_A\sigma_A) - \frac{1}{2}(\mu_A\mu_A|\lambda_A\sigma_A)\right] \end{aligned} \qquad (111)$$

2. Case $\mu \neq \nu,\quad A = B$

$$\begin{aligned} F_{\mu_A\nu_A} &= U_{\mu_A\nu_A} \\ &+ \sum_{C\neq A}\sum_{\lambda_C}\sum_{\sigma_C} P_{\sigma_C\lambda_C}\left[(\mu_A\lambda_C|\nu_A\sigma_C) - (\mu_A|V_C|\nu_A)\right] \\ &+ \sum_{\lambda_A}\sum_{\sigma_A} P_{\sigma_A\lambda_A}\left[(\mu_A\lambda_A|\nu_A\sigma_A) - \frac{1}{2}(\mu_A\nu_A|\lambda_A\sigma_A)\right] \end{aligned} \qquad (112)$$

3 Case $\mu \neq \nu,\quad A \neq B$

$$F_{\mu_A\nu_B} = \beta_{\mu_A\nu_B} - \frac{1}{2}\sum_{\lambda_A}\sum_{\sigma_B} P_{\sigma_B\lambda_A}(\mu_A\nu_B|\lambda_A\sigma_B) \qquad (113)$$

The NDDO approximation is distinguished from its CNDO and INDO counterparts in several ways. First, and most obvious, it includes more of the one and two-electron integrals necessary for a correct physical description. Thus, it is clearly a less drastic approximation to the full Roothaan-Hall equations. Most importantly perhaps, NDDO introduces a greater measure of directionality into the Fock matrix through the two-center, two-electron integrals and the nuclear attraction integrals since these are not spherically averaged as they are in the CNDO and INDO approximations. For CNDO and INDO, direction is imparted only through the resonance integrals, and then only indirectly in that they are set proportional to the orbital overlap.

More rigorously, the question of whether or not there exists a basis set for which the ZDO approximation is valid or almost valid has been studied by several investigators. Roby [23,24] has shown that, for the two-electron integrals at least, the NDDO approximation within a symmetrically orthogonalized minimal basis set is equivalent to the Rudenberg [25] approximation for integrals in the non-orthogonal atomic orbital basis. This conclusion seems to be supported by the calculations of Cook [26] and Brown [27]. No similar result could be found for the CNDO or INDO prescriptions for the treatment of these integrals.

However, it should be noted that these considerations in no way validate any approximate treatment of core Hamiltonian integrals. These must be considered separately and each on its own merit. This we shall have ample opportunity for in subsequent sections dealing with parameterization schemes and then again when examining the results

Parameterization Of Semi-Empirical Methods

The expressions for the elements of the Fock matrix within the CNDO, INDO, and NDDO methods derived in the preceding sections are essentially recipes for constructing the Fock matrix. They specify which integrals, or approximations to integrals must be considered to correctly implement a given level of approximation. However, they say nothing about how the values of these parameters are to be obtained. It is apparent, for example, that there must be a value for the term γ_{AB} representing all integrals of the form

$$(\mu_A\nu_B|\mu_A\nu_B) \qquad (114)$$

within the CNDO and INDO methods. But where should this value come from? Since this is a critical question in the implementation of any approximate method, it might be a good idea to point out what the choices are and what the motivation should be when making these choices

While it is clear that the objective of approximate methods is good results at a reduced computational expense, there remains the question of how "good results" are to be judged. Two obvious choices exist. The approximate results can be compared, at least in a qualitative sense, with 1) experiment or 2) *ab initio* results using either a similar or more complete basis It is the opinion of the author that the former is the preferred yardstick with the following explanation

There is little question as to the value of comparison with *ab initio* results when the goal is to test the validity of new or different approximations However, a method which agrees well with wrong *ab initio* results, no matter how aesthetically pleasing the method may be, will soon be supplanted in importance by a method which predicts and agrees with experimental results

Assuming that the goal is to obtain results which agree at least qualitatively with experiment, it is necessary to consider how the values which go into the previously derived expressions should be obtained. The first possibility, and in many ways perhaps the easiest, is that the integrals could simply be evaluated over the chosen basis set. However, given the approximate nature of these methods, such a non-empirical approach is likely to give results (a fortuitous cancellation of errors notwithstanding) which agree neither with *ab initio* results nor experiment.

Two other reasonable alternatives remain. The first is to take advantage of our considerable knowledge of molecules and select values which agree with their corresponding, experimentally determined quantities (although some consider this putting the cart before the horse in the sense that we end up predicting results a *posteriori*). The other and more pragmatic approach is simply to choose values which provide the desired results as determined, for example, by a least squares fit to a carefully selected set of data.

In practice a combination of all three of these alternatives are used. For instance, it is common to choose values for the atomic parameters $U_{\mu\mu}$ with reference to experimental ionization potentials and/or electron affinities; to evaluate the two-electron interactions explicitly (in some cases); and to choose the so called resonance integrals somewhat arbitrarily as a function of the overlap.

Before proceeding with any detailed discussion of parameterization schemes, it is useful to list those quantities which need to be determined before an SCF procedure can be carried out. These are summarized in table 1.

Table 1: Terms and integrals entering the CNDO, INDO, and NDDO Fock Matrix element expressions

Term	CNDO	INDO	NDDO
One-center atomic parameters	$U_{\mu\mu}$	$U_{\mu\mu}$	$U_{\mu\mu}$
Two-center, nuclear attraction integrals	V_{AC}	V_{AC}	$<\mu_A \vert V_C \vert \nu_A>$
One-center, two-electron integrals	γ_{AA}	$<\mu_A\nu_A \vert \sigma_A\lambda_A>$	$<\mu_A\nu_A \vert \sigma_A\lambda_A>$
Two-center, two-electron integrals	γ_{AB}	γ_{AB}	$<\mu_A\nu_B \vert \sigma_A\lambda_B>$
Two-center core Hamiltonian integrals	$\beta_{\mu_A\nu_B}$	$\beta_{\mu_A\nu_B}$	$\beta_{\mu_A\nu_B}$

One-Center, Two-Electron Integrals

The atomic two-electron integrals formed from Slater-type orbitals can be evaluated by partitioning the integral into its angular and radial parts. When this is done the integral is expressed in terms of sums of radial integrals, each term of which is multiplied by a particular numerical factor arising from the integral's angular component. The radial integrals are known as Slater-Condon [28] factors and their angular multipliers are given by the Clebsch-Gordon coefficients [29].

These factors are of great utility in the parameterization of semi-empirical methods because they allow for a reduction in the number of parameters per atom. For example, the six unique two-electron integrals arising from a valence-only s,p basis set for a second row atom can be expressed in terms of three Slater Condon factors according to[4]

$$(ss|ss) = (sp_\mu|sp_\mu) = F^0(s,s) \tag{115a}$$

$$(sp_\mu|p_\mu s) = \frac{1}{3}G^1(s,p) \tag{115b}$$

$$(p_\mu p_\mu|p_\mu p_\mu) = F^0 + \frac{4}{25}F^2(p,p) \tag{115c}$$

$$(p_\mu p_\nu|p_\mu p_\nu) = F^0 - \frac{2}{25}F^2(p,p) \tag{115d}$$

$$(p_\mu p_\nu|p_\nu p_\mu) = \frac{3}{25}F^2(p,p) \tag{115e}$$

The Slater-Condon F's and G's can be calculated given the radial component of the orbitals. This is typically done for F^0. However, one of the requirements of a method which does not neglect one-center exchange is that it accurately reproduce atomic term energy differences. This requirement is better met, in general, by using the so-called "experimental" Slater-Condon factors which are generated from a least squares fit to experimental energy levels. Thus, the experimental Slater-Condon factors simplify the process of parameterizing semi-empirical methods and are used in conjunction with ionization potentials and electron affinities in the determination of the atomic core parameters to be discussed in the next section.

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[4] Note that the 2s and 2p orbitals are assumed to have the same radial function.

One-Center (Atomic) Core Parameters

The one-center integrals of the core Hamiltonian,

$$U_{\mu_A\mu_A} = \langle\mu_A| - \frac{1}{2}\nabla^2 - \frac{Z'_A}{R_A}|\mu_A\rangle \qquad (116)$$

represent the kinetic and potential energy of an electron in the orbital φ_μ, on atom A, in the electrostatic field generated by A's valence charge. These terms could be evaluated explicitly over the atomic orbital basis and adjusted for use in semi-empirical calculations via a core pseudo-potential [30,31]. However, they are almost always treated as empirical parameters with values determined from atomic spectroscopy.

To do this in a manner which does not favor one spectroscopic state of an atom over another it is reasonable to use the average energy of a given electronic configuration. This quantity is the weighted mean of the energies of the spectroscopic terms arising from the configuration For example, the electronic configuration $1s^22s^22p^2$ has the average energy

$$\overline{E}(1s^22s^22p^2) = \frac{E(^1S) + 5E(^1D) + 9E(^3P)}{15} \tag{117}$$

In general, the energy of an atomic term can be expressed in terms of the core integrals $U_{\mu\mu}$ and the two-electron Coulomb and exchange integrals As was shown in the previous section, the Coulomb and exchange integrals can in turn be expressed in terms of Slater-Condon factors Thus, it is possible to express the average energy of an atomic configuration in these same terms The expression is obtained by summing the U's for each electron and then adding the sum, over electron pairs, of the average pairwise two-electron interaction energies [32] i.e

$$\overline{E} = \sum_i U_{ii} + \sum_{i<j} \overline{\langle ij||ij\rangle} \tag{118}$$

For a valence *2s2p* atomic configuration the only possible pairwise interactions are

$$\overline{\langle ss|ss\rangle} = F^0 \tag{119a}$$

$$\overline{\langle pp|pp\rangle} = F^0 - \frac{2}{25}F^2 \tag{119b}$$

$$\overline{\langle sp|sp\rangle} = F^0 - \frac{1}{6}G^1 \tag{119c}$$

which lead to

$$\begin{aligned}\overline{E}(2s^m2p^n) = mU_{2s\,2s} + nU_{2p,2p} + \frac{1}{2}(m+n)(m+n-1)F^0 \\ -\frac{1}{6}mnG^1 - \frac{1}{25}n(n-1)F^2\end{aligned} \tag{120}$$

for the average energy of the configuration having *m* *s*-electrons and *n* *p*-electrons

Using these configuration averaged energies, the ionization potential or electron affinity for an *s* or *p* electron is given by

$$I_{2s}(A) = \overline{E}_{A^+}(2s^{m-1}2p^n) - \overline{E}_A(2s^m2p^n) \tag{121a}$$

$$I_{2p}(A) = \overline{E}_{A^+}(2s^m2p^{n-1}) - \overline{E}_A(2s^m2p^n) \tag{121b}$$

$$A_{2s}(A) = \overline{E}_A(2s^m2p^n) - \overline{E}_{A^-}(2s^{m+1}2p^n) \tag{121c}$$

$$A_{2p}(A) = \overline{E}_A(2s^m2p^n) - \overline{E}_{A^-}(2s^m2p^{n+1}) \tag{121d}$$

which provide four equations for the determination of five atomic parameters However, we have already noted that F^0 is usually evaluated analytically over a basis of Slater type *s* orbitals and the remaining *F*'s and *G*'s are taken from experiment, making it possible to determine *U*'s either from IP's alone or from an average of IP's and EA's as Pople did in his CNDO/2 model.

Two-Center, One-Electron Integrals

The integral V_{AB} is not difficult to evaluate analytically over a basis of STO's and this, In fact, was done in the original CNDO/1 parameterization However, CNDO/1 tended to produce bond lengths which were too short and correspondingly too high dissociation energies. Pople traced this problem to a so-called penetration effect described by the term $Z_B\gamma_{AB} - V_{AB}$ which arises if the two-center terms of Eq (95) are rewritten as

$$(Z_B\gamma_{AB} - V_{AB}) - Q_B\gamma_{AB} \tag{122}$$

where

$$Q_B = Z_B - P_{BB} \tag{123}$$

describes the net charge on center B This deficiency in the method was corrected in the simplest possible way by setting V_{AB} equal to $Z'_B\gamma_{AB}$ thereby forcing the penetration term to vanish and establishing the commonly used approximation for the two-center nuclear-electronic attraction integrals.

Two-Center, Two-Electron Integrals

Various schemes have been used for these integrals and several important ones are briefly outlined below

Analytical

In the original CNDO/1 parameterization the two-center Coulomb integrals, γ_{AB} were evaluated analytically according to the formulae given by Roothaan [33]

Mataga-Nishimoto

The Mataga Nishimoto formula [34] is

$$\gamma_{AB} = \frac{1}{a + R_{AB}} \tag{124}$$

where

$$a = \frac{\gamma_{AA} + \gamma_{BB}}{2} \tag{125}$$

and $\gamma_{AA} = I_A + A_A$ is the relation adopted by Pariser [35] based on experience gained from π-electron calculations

A modified Mataga-Nishimoto formula having the form

$$\gamma_{AB} = \frac{f_\gamma}{\frac{2f_\gamma}{(\gamma_{AA}+\gamma_{BB})} + R_{AB}} \tag{126}$$

was employed by Ridley and Zerner [36] The value of f_γ was chosen to reproduce the spectrum of benzene and has the effect of raising the value of the integrals above those obtained from Eq (124).

Ohno-Klopman

For the various MINDO parameterizations [37–44], Dewar *et al* adopted the Ohno-Klopman formula [45]

$$\gamma_{AB} = \left[R_{AB}^2 + \frac{1}{2}\left(\frac{\gamma_{AA}+\gamma_{BB}}{\gamma_{AA}\gamma_{BB}}\right)^2\right]^{-\frac{1}{2}} \tag{127}$$

where γ_{AA} and γ_{BB} are average one-center Coulomb integrals

Two-Center, One-Electron Matrix Elements

These are the so-called resonance integrals usually obtained from

$$\beta_{\mu_A\nu_B} = \frac{1}{2}(\beta_A + \beta_B)S_{\mu\nu}K_x \quad \{x = \sigma, \pi\} \tag{128}$$

where B_A and B_B are determined empirically via a least squares fit to data chosen for a specific model (spectra versus geometry, for example)

Summary

I have attempted to give an overview of all-valence semi-empirical methods by describing the fundamental expressions obtained for the Fock matrix through a consistent and rotationally invariant application of the ZDO approximation. While I have very briefly touched upon the topic of how such approximate methods are parameterized, I have by no means given an exhaustive review of parameterization schemes. Over the years many such schemes have been introduced and several excellent reviews of these schemes have appeared in the literature. Since it would be rather superfluous to reproduce another such review, the interested reader is referred to the broad base of existing literature [46-51].

The CNDO, INDO, and NDDO integral approximations and their corresponding SCF schemes are undoubtedly well established. The neglect of integrals and the introduction of parameters from atomic spectroscopy seem very well founded based on the accuracy of the results obtained. The main weaknesses in these methods then appear to stem from one or all of the following:

1. The formulation of the resonance integral
2. The evaluation of the nuclear-electronic attraction integrals as equivalent to the corresponding two-electron repulsion integral
3. Neglect of two-center core-valence repulsion
4. The formulation of the two-center Coulomb integrals
5. The assumption that a minimum basis set with a parameterized Hamiltonian can accurately reproduce experiment
6. Neglect of three-center terms

Of these, the formulation of the resonance integrals, based, as they are, on pure parameters, seems a likely point of attack in an attempt to improve our approximate Hamiltonian. The very simple form for $\beta_{\mu_A\nu_B}$ chosen by Pople and his coworkers in the original CNDO/1 parameterization is based on a formula used by Wolfsberg and Helmholz [52] in Extended Hückel type calculations on tetrahedral ions. The appeal of such a formula rests in the fundamental notion that the bonding parameters should be proportional to the overlap of atomic orbitals. This concept is consistent with the chemist's intuitive understanding of the chemical bond as composed of electrons shared among atomic nuclei.

In Extended Hückel type theories one can show that the largest off diagonal elements of the Hamiltonian should be proportional to the overlap by using the Mulliken integral approximation [53]

$$(\mu\nu| \approx S_{\mu\nu}\frac{(\mu\mu| + (\nu\nu|}{2} \tag{129}$$

In ZDO theories a similar proportionality is suggested by the symmetrical orthogonalization of the basis using a binomial expansion of the overlap, i.e.,

$$\mathrm{X}^{L} = \mathrm{X}S^{-\frac{1}{2}} \tag{130}$$

and

$$S^{-\frac{1}{2}} = (1+\Delta)^{-\frac{1}{2}} = 1 - \frac{1}{2}\Delta + \tag{131}$$

However, in this case the relationship to the Slater basis is uncertain. Furthermore, the expansion of $\mathbf{S}^{-\frac{1}{2}}$ is divergent since many of the elements of $\mathbf{S}$ are greater than about 0.25 for an all valence basis set.

Other formulas, most of which are modifications of the Wolfsberg-Helmholz formula, have been introduced. These have usually consisted of additional parameters. For example, Del Bene and Jaffe [54, 55] introduced a multiplicative factor for scaling the π-π interactions. The formula thus took the form

$$\beta_{\mu_A \nu_B} = \frac{\beta_A + \beta_B}{2} K_{\mu\nu} S_{\mu\nu} \tag{132}$$

where $K_{\sigma\sigma} = 1$ and $K_{\pi\pi} = 0.585$. Ridley and Zerner [36] used the same formula but set $K_{\sigma\sigma} = 1.266$ and noted that such scaling can be justified from an examination of *ab initio* calculations.

The general form

$$\beta_{\mu_A \nu_B} = S_{\mu\nu}(I_\mu^A + I_\nu^B) f(R_{AB}) \tag{133}$$

where I_μ^A is the appropriate valence state ionization potential for an electron in orbital μ on atom A, was chosen by Dewar and his coworkers for MINDO. In MINDO/1 the function $f(R_{AB})$ was set to

$$f(R_{AB}) = A_{AB} + \frac{B_{AB}}{R_{AB}^2} \tag{134}$$

with the parameters A_{AB} and B_{AB} chosen for each pair of atoms to properly reproduce molecular heats of formation. For MINDO/2 and MINDO/3, $f(R_{AB})$

was given by a single parameter, C_{AB}, for each atom pair with optimal values determined from a least squares fit to a series of reference molecules. More recent methods such as MNDO [56], AM1 [57], and PM3 [58,59] use similar schemes but tend to be more highly parameterized.

It should also be mentioned that much of the success of the schemes utilizing these formulas has been in the area of spectroscopy (Eq. (132)) and thermodynamic properties (Eq. (133)). Other molecular properties, most notably geometries, are often poorly predicted. The most notable example of which is the tendency of ZDO based methods to favor the more highly bonded structure of two isomers. However, this problem is not attributed to the resonance integral formulations so much as the neglect of so many two-electron repulsions that the remaining integrals, primarily nuclear attraction integrals, are given too much weight. Whether this deficiency can be compensated for by an alternative resonance integral formulation is doubted.

More relevant to the current discussion is the indictment handed down by de Bruijn [60] charging that schemes which set β proportional to the overlap are correct only for diatomic molecules or nearest-neighbor interactions in polyatomic molecules. De Bruijn further states that formulas for non-neighboring atoms must include parameters which take explicit account of the geometry of the molecule. However, his case was based on a divergent expansion of $\mathbf{S}^{-\frac{1}{2}}$ and his suggestions for alternative forms for β would force a larger parameter space on the method and/or introduce complications which outweigh their benefits.

Nonetheless, in cases where the expansion is appropriate, for example π electron calculations on benzene, it is pointed out that the sign of β between non-nearest neighbors is impossible to predict and may very well be positive. This conclusion is supported in part by the calculations of Chong [61] who found $\beta_{13}^{C} = +0.07\ eV$ for benzene. It is clear that positive values are inconsistent with the prescriptions for β used in currently popular ZDO methods which suggest only negative values (assuming a positive overlap). These facts constitute the motivation for an alternative form for the resonance integral which shall be taken up in the next chapter.

CHAPTER 3
RESONANCE INTEGRALS

Introduction

Reasoning that parameterization schemes in semi-empirical methods "should be subjected to certain boundary conditions derived from basic quantum mechanical postulates", Linderberg [62] derived formulas for resonance integrals within the Pariser-Pople-Parr [51, 63–67] method by making use of the equivalency of the dipole length and dipole velocity operators. These formulas gave values which were well within the range of those obtained from empirical parameters in conjunction with Mulliken or Wolfberg Helmholz-like formulas and proved to be of practical use in a broad range of applications including electronic spectra, spin densities [68–72], optical activity [73, 74] and metal band structure [75].

Linderberg and Seamans [76] extended the method for valence-only *s,p* basis sets and pointed out that the simple one-to-one correspondence between momentum matrix elements and two-center core Hamiltonian matrix elements disappears due to a coupling generated by the off-diagonal, one-center position matrix elements. Lipinski and coworkers have incorporated these formulas into a valence-only INDO method which has successfully reproduced ground and excited state properties of a wide range of molecules [77–82]. Lipinski and Leszczynski subsequently extended the method further to include d orbitals [83] and Rydberg orbitals [84]

In this work the resonance integral formulas of Linderberg and Seamans are used for the two-center core Hamiltonian matrix elements in an NDDO level semi-empirical method. General applicability to prediction of molecular spectra and geometries are investigated and comparisons with respect to INDO results and experiment are presented.

What follows is the detailed derivation for an s,p basis set.

Derivation

The Hamiltonian

The starting point of this development is the equation of motion for the position operator in the Heisenberg formulation of quantum mechanics where the time evolution of a physical system is viewed as change in the dynamical variables with time [85], the state vectors remaining fixed.

$$i\hbar\frac{d\mathbf{r}}{dt} = i\hbar\frac{\mathbf{p}}{m} = [\mathbf{r}, H] \tag{135}$$

If H is the many-electron Hamiltonian which is assumed to be of the form

$$H = h + g \tag{136}$$

where h and g are the one and two-electron contributions to the Hamiltonian, respectively, then the commutator is given by

$$[\mathbf{r}, H] = [\mathbf{r}, h] + [\mathbf{r}, g] \tag{137}$$

We expect that at an exact level of theory the dipole velocity will be a one-electron operator [86] and consequently any two-electron contributions will vanish,

$$[\mathbf{r}, g] = 0 \tag{138}$$

While Eq. (138) certainly holds for the exact many-electron Hamiltonian and a complete basis, it is also true that the use of an approximate Hamiltonian or a truncated basis or both will, in all likelihood, invalidate Eq. (138). And, in fact, some authors have raised objections to the Linderberg Seamans formulas based on this point, since in practice H is usually the Fock operator and the basis sets are rarely complete. Nonetheless, as Linderberg pointed out, the derivations are only rigorous if the assumptions, of which Eq. (138) is one, are accepted.

In light of Eq. (138) we now have

$$i\hbar\frac{\mathbf{p}}{m} = [\mathbf{r}, h] \tag{139}$$

which, after introduction of a basis and conversion to atomic units yields

$$i\,\langle\mu_A|\mathbf{p}|\nu_B\rangle = \langle\mu_A|[\mathbf{r}, h]|\nu_B\rangle \tag{140}$$

As is often the case it is useful to expand the commutator above via the familiar resolution of the identity to obtain

$$i\,\langle\mu_A|\mathbf{p}|\nu_B\rangle = \sum_{\lambda}\langle\mu_A|\mathbf{r}|\lambda\rangle\langle\lambda|h|\nu_B\rangle - \langle\mu_A|h|\lambda\rangle\langle\lambda|\mathbf{r}|\nu_B\rangle \tag{141}$$

Eq. (141) now becomes the focal point of this chapter since it relates matrix elements of the position and momentum operators to those of the core Hamiltonian. The following sections will develop approximations which will simplify this relationship and lead to useful expressions for the core Hamiltonian matrix elements.

Position Operator Matrix Elements

We are now interested in matrix elements of the position operator over an orthogonal set of s,p type atomic orbitals. Rewriting $\mathbf{r}$ as

$$\mathbf{r} = \mathbf{R}_A + \mathbf{r} - \mathbf{R}_A \tag{142}$$

and invoking ZDO at the NDDO level of approximation gives

$$\langle \mu_A | \mathbf{r} | \nu_B \rangle = \delta_{AB} [\delta_{\mu\nu} \mathbf{R}_A + \langle \mu_A | \mathbf{r} - \mathbf{R}_A | \nu_A \rangle] \tag{143}$$

where the $\delta_{\mu\nu}$ arises from the orthogonality of the basis set. It should be noted that, rigorously, the two-center matrix elements of the position operator do not vanish within the NDDO approximation since $\mathbf{r}$ is not a spherically symmetric operator. However, experience has shown that such integrals have little effect on the calculation of properties such as transition moments and polarizabilities [87] so that neglecting them is not unjustified. Thus Eq. (143) becomes, in essence, a working definition of ZDO in the current context and as such is another assumption of the development. Substitution of Eq. (143) into the right-hand side of Eq.

(141) gives (see appendix D)

$$
\begin{aligned}
i\langle\mu_A|\mathbf{p}|\nu_B\rangle = (\mathbf{R}_A - \mathbf{R}_B)\langle\mu_A|h|\nu_B\rangle \\
+\ \mathbf{e}_x\,[u_A(\delta_{\mu_A s_A}\langle x_A|h|\nu_B\rangle + \delta_{\mu_A x_A}\langle s_A|h|\nu_B\rangle) \\
-u_B(\delta_{\nu_B s_B}\langle\mu_A|h|x_B\rangle + \delta_{\nu_B x_B}\langle\mu_A|h|s_B\rangle)\,] \\
+\ \mathbf{e}_y\,[u_A(\delta_{\mu_A s_A}\langle y_A|h|\nu_B\rangle + \delta_{\mu_A y_A}\langle s_A|h|\nu_B\rangle) \\
-u_B(\delta_{\nu_B s_B}\langle\mu_A|h|y_B\rangle + \delta_{\nu_B y_B}\langle\mu_A|h|s_B\rangle)\,] \\
+\ \mathbf{e}_z\,[u_A(\delta_{\mu_A s_A}\langle z_A|h|\nu_B\rangle + \delta_{\mu_A z_A}\langle s_A|h|\nu_B\rangle) \\
-\ u_B(\delta_{\nu_B s_B}\langle\mu_A|h|z_B\rangle + \delta_{\nu_B z_B}\langle\mu_A|h|s_B\rangle)\,]
\end{aligned}
\tag{144}
$$

which motivates an examination of the two-center linear momentum matrix elements to be taken up in the next section

Two-Center Momentum Matrix Elements

We now wish to determine the general form of the two-center linear momentum matrix. In order to keep the treatment as simple as possible we will consider a diatomic molecule, *A-B* in a coordinate system where *A* is at the origin and *B* on the *z* axis at a distance *R* from *A*. If we now consider the transformation properties the momentum operator and the basis functions under the $C_{\infty v}$ point group, we find that the *s*, and p_z basis functions and the operators $\mathbf{p}_z$ transform as the totally symmetric (A_1) irreducible representation (irrep) while $p_x, p_y, \mathbf{p}_x$, and $\mathbf{p}_y$ transform as the E_1 or π irrep. Noting that

$$E_1 \otimes E_1 = E_2 + A_1 + A_2 \qquad \{C_{\infty v}\} \tag{145}$$

the following generalized matrix representation of $\mathbf{p}$ can be verified.

$$i\,\langle\mu_A|\mathbf{p}|\nu_B\rangle = \begin{bmatrix} \nabla_{ss}\mathbf{e}_z & \nabla_{s\pi}\mathbf{e}_x & \nabla_{s\pi}\mathbf{e}_y & \nabla_{s\sigma}\mathbf{e}_z \\ \nabla_{\pi s}\mathbf{e}_x & \nabla_{\pi\pi}\mathbf{e}_z & 0 & \nabla_{\pi\sigma}\mathbf{e}_x \\ \nabla_{\pi s}\mathbf{e}_y & 0 & \nabla_{\pi\pi}\mathbf{e}_z & \nabla_{\pi\sigma}\mathbf{e}_y \\ \nabla_{\sigma s}\mathbf{e}_z & \nabla_{\sigma\pi}\mathbf{e}_x & \nabla_{\sigma\pi}\mathbf{e}_y & \nabla_{\sigma\sigma}\mathbf{e}_z \end{bmatrix} \qquad (146)$$

An analogous treatment of the core Hamiltonian yields

$$\langle\mu_A|h|\nu_B\rangle = \begin{bmatrix} \beta_{ss} & 0 & 0 & \beta_{s\sigma} \\ 0 & \beta_{\pi\pi} & 0 & 0 \\ 0 & 0 & \beta_{\pi\pi} & 0 \\ \beta_{\sigma s} & 0 & 0 & \beta_{\sigma\sigma} \end{bmatrix} \qquad (147)$$

Comparing vector components among Eqs. (144), (146) and (147) the following relations are obtained

$$\nabla_{ss} = -R\beta_{ss} + u_A\beta_{\sigma s} - u_B\beta_{s\sigma} \qquad (148a)$$

$$\nabla_{s\pi} = u_A\beta_{\pi\pi} - u_B\beta_{ss} \qquad (148b)$$

$$\nabla_{s\sigma} = -R\beta_{s\sigma} + u_A\beta_{\sigma\sigma} - u_B\beta_{ss} \qquad (148c)$$

$$\nabla_{\pi s} = u_A\beta_{ss} - u_B\beta_{\pi\pi} \qquad (148d)$$

$$\nabla_{\pi\pi} = -R\beta_{\pi\pi} \qquad (148e)$$

$$\nabla_{\pi\sigma} = u_A\beta_{s\sigma} \qquad (148f)$$

$$\nabla_{\sigma s} = -R\beta_{\sigma s} + u_A\beta_{ss} - u_B\beta_{\sigma\sigma} \qquad (148g)$$

$$\nabla_{\sigma\pi} = -u_B\beta_{\pi s} \qquad (148h)$$

$$\nabla_{\sigma\sigma} = -R\beta_{\sigma\sigma} + u_A\beta_{s\sigma} - u_B\beta_{\sigma s} \qquad (148i)$$

The equations Eq. (148a) through Eq. (148i) constitute an overdetermined system of equations for the five β's in terms of the nine $\nabla_{\mu\nu}$'s. It has been suggested that the β's determined from a least-squares fitting procedure Linderberg felt, and the current author agrees, that such a procedure is not very aesthetically pleasing Rather, we shall proceed, as Linderberg did, to find relationships among the del parameters which will reduce their number.

Reduction of Linear Momentum Matrix Elements

From the symmetry of Slater-type (or any central field type) p orbitals we have

$$p_x|p_x > \;=\; \hat{p}_z|p_z > \qquad (149)$$

which implies that

$$\nabla_{\sigma\pi} = \nabla_{\pi\sigma} = \nabla_{\pi\pi} \qquad (150)$$

and when combined with Eqs (148e), (148f), and (148h) gives

$$R\beta_{\pi\pi} = \; -u_A\beta_{s\sigma} = \; u_B\beta_{\sigma s} \qquad (151)$$

Furthermore it can be shown (though not without some effort–see appendix D for a derivation of the first of these) that

$$\nabla_{s\sigma} = \frac{d}{dR}(R\nabla_{s\pi}) \qquad (152)$$

and

$$\nabla_{\sigma\sigma} = \frac{1}{R}\;\frac{d(R^2\nabla_{\pi\pi})}{dR} \qquad (153)$$

which together with Eq (150) reduce the number of ∇ parameters to five We can now make use of Eqs (148a)–(148i) and Eqs (151)-(153) in a series of successive eliminations to produce expressions containing only the five betas and the two atomic transition moments

Beginning with Eq (148i) and combining it with Eq (153) and Eq (150) yields

$$\frac{1}{R}\frac{d(R^2\nabla_{\pi\pi})}{dR} = -R\beta_{\sigma\sigma} - 2R\beta_{\pi\pi} \tag{154}$$

which can be expanded to

$$R\frac{d\nabla_{\pi\pi}}{dR} + 2\nabla_{\pi\pi} = -R\beta_{\sigma\sigma} - 2R\beta_{\pi\pi} \tag{155}$$

Substituting Eq (148e) into Eq (155) gives

$$R\frac{d\nabla_{\pi\pi}}{dR} - 2RB_{\pi\pi} = -R\beta_{\sigma\sigma} - 2R\beta_{\pi\pi} \tag{156}$$

which, after rearranging leaves

$$\beta_{\sigma\sigma} = \frac{-d\nabla_{\pi\pi}}{dR} = \frac{d(R\beta_{\pi\pi})}{dR} \tag{157}$$

Proceeding now with Eq (148c), we can rearrange it and perform the substitutions suggested by Eqs (157) and (152) as follows,

$$\beta_{\sigma\pi} = \frac{1}{R}\left[u_A\beta_{\sigma\sigma} - \nabla_{\sigma\sigma} - u_B\beta_{\pi\pi}\right] = \frac{1}{R}\left[u_A\frac{d(R\beta_{\pi\pi})}{dR} - \frac{d(R\nabla_{\sigma\pi})}{dR} - u_B\beta_{\pi\pi}\right] \tag{158}$$

Using Eq. (148b) to replace $\nabla_{s\pi}$ leads to

$$\begin{aligned}\beta_{s\sigma} &= \frac{1}{R}\left[u_A\frac{d(R\beta_{\pi\pi})}{dR} - \frac{d[R(u_A\beta_{\pi\pi} - u_B\beta_{s\sigma})]}{dR} - u_B\beta_{ss}\right] \\ &= \frac{1}{R}\left[u_A\frac{d(R\beta_{\pi\pi})}{dR} - u_A\frac{d(R\beta_{\pi\pi})}{dR} + u_B\frac{d(R\beta_{s\sigma})}{dR} - u_B\beta_{ss}\right] \\ &= \frac{1}{R}\left[u_B\frac{d(R\beta_{s\sigma})}{dR} - u_B\beta_{ss}\right] \qquad (159)\end{aligned}$$

Finally, differentiation yields

$$\beta_{s\sigma} = \frac{1}{R}\left[u_B R\frac{d(\beta_{s\sigma})}{dR} + u_B\beta_{s\sigma}\frac{d(R)}{dR} - u_B\beta_{ss}\right] = \frac{d(u_B\beta_{s\sigma})}{dR} \qquad (160)$$

and similarly for

$$\beta_{\pi s} = -\frac{d(u_A\beta_{ss})}{dR} \qquad (161)$$

For $\beta_{\pi\sigma}$ we began with Eq. (148e) and then use Eqs. (150), (148f), (160) as follows

$$\begin{aligned}\beta_{\pi\pi} &= -\frac{1}{R}\nabla_{\pi\pi} \\ &= -\frac{1}{R}\nabla_{\pi\sigma} \\ &= -\frac{1}{R}u_A\beta_{s\sigma} \\ &= -\frac{1}{R}\frac{d(u_Au_B\beta_{ss})}{dR} \qquad (162)\end{aligned}$$

Finally, $\beta_{\sigma\sigma}$ can be obtained using the previous results, namely Eqs (157) and (162) to arrive at

$$\beta_{\sigma\sigma} = -\frac{d^2(u_A u_B \beta_{ss})}{dR^2} \tag{163}$$

At this point the beta parameters can be completely determined from the single function β_{ss} hence, its choice is a key element of any method based on this development. Linderberg and Seamans noted that comparison of Eq (162) with

$$\beta_{\mu\nu} = \frac{1}{R}\frac{dS_{\mu\nu}}{dR} \tag{164}$$

which arises from the nonzero z component of the gradient matrix along the internuclear axis, suggests the choice of

$$S_{\pi\pi} \cong -u_A u_B \beta_{ss} \tag{165}$$

It is now possible to express all the resonance integrals in terms of first and second derivatives of the π-π overlap as follows to obtain the final expressions below

$$\beta_{ss} = \frac{-S_{\pi\pi}}{u_A u_B} \tag{166a}$$

$$\beta_{s\sigma} = \frac{-S'_{\pi\pi}}{u_A} \tag{166b}$$

$$\beta_{\sigma s} = \frac{S'_{\pi\pi}}{u_B} \tag{166c}$$

$$\beta_{\sigma\sigma} = S''_{\pi\pi} \tag{166d}$$

$$\beta_{\pi\pi} = \frac{S'_{\pi\pi}}{R} \tag{166c}$$

The equations pertaining to the case in which one of the two atoms has only an s orbital and the other both s and p functions and the case where each atom has only an s function are obtained in a similar fashion and are given by

$A(s) - B(s, p)$

$$\beta_{ss} = \frac{S_{s\sigma}}{u_p R} \tag{167a}$$

$$\beta_{s\sigma} = \left(\frac{S_{s\sigma}}{R}\right)' \tag{167b}$$

$A(s) - B(s)$

$$\beta_{ss} = \frac{S'_{ss}}{R} \tag{168}$$

CHAPTER 4
PROCEDURES AND RESULTS

General Parameterization

The general expressions for the Fock matrix elements within the NDDO approximation have been previously described as has the general method for parameterizing semi-empirical methods. Therefore the following discussion is limited to the details specific to the INDO and NDDO implementations adopted in this work.

The atomic parameters, $U_{\mu\mu}$, were the same for both the INDO and NDDO calculations which seems reasonable since the expression for the average energy of an atomic configuration is the same for each of the two approximations. The values chosen were based on ionization potentials and are essentially those of Ridley and Zerner [36]. This set of parameters has proven reliable over time and there seems to be little evidence that further modifications would prove beneficial.

For INDO the so-called neglect of penetration approximation $V_{AB} = Z'_B\gamma_{AB}$ was kept as it provides an effective means of compensating for the assumption of an orthogonal basis. The actual calculation of this term using a non-orthogonal basis tends to produce nuclear attraction terms which are too large. In the NDDO case the spirit of the neglect of penetration was used, but in a manner consistent with the NDDO approximation Thus, these terms were calculated according to the approximation of Geoppert-Mayer and Sklar [88] as

$$\langle \mu_A | \frac{Z_B}{r} | \nu_A \rangle = Z_B \langle \mu_A s_B | \frac{1}{r} | \nu_A s_B \rangle \tag{169}$$

where $s_B(2)s_B(2)$ is chosen as a spherically averaged charge distribution at center B It is readily apparent that for CNDO and INDO this reduces to and is consistent with $V_{AB} \simeq Z'_B \gamma_{AB}$

The INDO two-electron integrals are taken from the semi-empirical Slater-Condon factors for the one-center case and approximated as

$$\langle \mu_A \nu_B | \mu_A \nu_B \rangle \simeq \langle s_A s_B | s_A s_B \rangle = \gamma_{AB} \tag{170}$$

for the two-center case. For NDDO, all two-electron integrals are evaluated analytically over STO-3G expansions [89] of the Slater-type orbital basis functions Almlof's *VMOL* [90] integral package was modified and used for the evaluation of these integrals

Resonance Integrals

Figures 1 through 4 plot resonance integral (β) values of N_2 as a function of the internuclear separation In each of the four graphs the first curve (marked by an asterisk) corresponds to the standard Wolfsberg-Helmholz (WH) formula with β^0_N = -25 0 eV, f_σ = 1.267 and f_π = 0.585 The second curve (marked by a triangle) corresponds to the Landerberg-Seamans (LS) formula for the appropriate β Given the seemingly different functional forms of these equations, the similarity in the resulting curves is rather remarkable. In each case the two curves intersect in the vicinity of the bonding region (approximately 1.1 Å for N_2) but have notably different slopes and curvatures which should lead to differing bond lengths and force constants. It is interesting to note that the original equation of motion formalism for resonance integrals was developed by Linderberg [62] for the π only PPP method in which only nearest neighbor interactions are considered. In light of figure 4, its success in this area is not surprising. Also worthy of mention is the fact that given the close correspondence of $\beta_{\pi\pi}$ within the two methods, the π-π interaction factor of 0.585, found to be crucial to the accurate prediction of electronic spectra, seems to be inherent in the LS formulas. Based on these figures we can expect the LS formulas to yield resonance integral values in a generally useful range. Whether these values will lead to the accurate prediction of molecular properties within an approximate, semi-empirical framework is the subject of subsequent sections of this chapter.

Before proceeding to examine this question in more detail I would like to comment briefly on figure 5 which shows clearly that the LS scheme produces values for β as a function of R close to the conventional schemes which set β proportional to the overlap. This graph further illustrates the need for different weights (interaction factors) for each of the four interactions displayed. This is in addition to the 0.585 factor often used for the π interaction when β is set proportional to the overlap. The oscillation in the σ-σ curve is the result of this interaction crossing the axis (figure 3), where the interaction itself is small. In most cases this fluctuation is unimportant and occurs inside of the equilibrium bond distance.

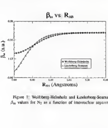

Figure 1: Wolfsberg-Helmholz and Linderberg-Seamans β_{aa} values for N_2 as a function of internuclear separation.

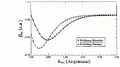

Figure 2 Wolfsberg-Helmholz and Linderberg-Seamans $\beta_{s\sigma}$ values for N_2 as a function of internuclear separation.

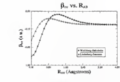

Figure 3 Wolfsberg-Helmholz and Linderberg-Seamans $\beta_{\sigma\sigma}$ values for N_2 as a function of internuclear separation

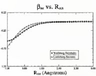

Figure 4 Wolfsberg-Helmholz and Lindeberg-Seamans $\beta_{\pi\pi}$ values for N_2 as a function of internuclear separation.

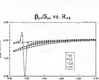

Figure 5 Pure β parameters as determined from the Linderber-Seamans formulas as a function of the internuclear separation.

INDO vs. NDDO Matrix Elements

One of the most important aspects in the development of an approximate, semi-empirical method is the delicate balance of electrostatic terms in the Hamiltonian. It has already been mentioned that the exact calculation of nuclear-electronic attraction integrals in the original CNDO/1 method led to an approximate Hamiltonian in which this balance was not quite preserved. The consequences were, in general, the prediction of bond distances which were too short and, more specifically, to such phenomena as a bound first triplet state of H_2.

Pople attributed this problem to the penetration of the core of atom B by electrons in orbitals on atom A. This can be seen by rewriting

$$\sum_{C \neq A} (P_{CC}\gamma_{AC} - V_{AC}) \tag{171}$$

as

$$\sum_{C \neq A} (P_{CC} - Z_C)\gamma_{AC} + \sum_{C \neq A} (Z_C\gamma_{AC} - V_{AC}) \tag{172}$$

We then have

$$P_{CC} - Z_C = -(Z_C - P_{CC}) = -Q_C \tag{173}$$

where Q_C is the net charge on center C. Following Goeppert-Mayer and Sklar [88] $Z_C\gamma_{AC}$, can be considered an approximation to the nuclear attraction integral V_{AC}. In this case the terms in the second sum of Eq. (172) can be thought of as an excess nuclear-electronic attraction, or penetration effect, which can be conveniently neglected by setting $V_{AC} \equiv Z_C\gamma_{AC}$ Viewed another way, the assumption of an orthogonal basis is not compatible with the analytical calculation of nuclear-electronic attraction integrals over a non-orthogonal STO basis Calculation of the nuclear attraction terms followed by a correction for the core pseudo-potential and symmetric orthogonalization does, in fact, lead to $V_{AC} \approx Z_C\gamma_{AC}$ [91] which seems to adequately compensate for this error, *a posteriori*.

In light of this discussion it is reasonable to ask whether the analogous correction within the NDDO method implemented in this work maintains the balance of the semi-empirical Hamiltonian. Table 2 gives a term by term breakdown of the one-center Fock matrix elements of N_2 within the INDO and NDDO methods[5] Neglecting momentarily the s-p_z element, the spherical nature of the INDO gammas is readily apparent as the $Z_B\gamma_{AB}$ INDO terms, which are the average of the corresponding NDDO terms. It is also apparent that the inclusion of NDDO type integrals provides a more accurate representation of the anisotropy of the nuclear attraction and two-electron contributions to the Fock matrix

The NDDO s-p_z Fock element which has no one-electron contribution at the INDO level, is roughly four times smaller than its INDO counterpart. Although the NDDO integrals give rise to a large two-electron contribution this effect is more than compensated for by the one-electron $Z_B(\mu\nu|ss)$ term resulting in the overall smaller matrix element. These off-diagonal elements however, are small compared to the diagonal elements and their effect on the resulting wavefunction does not appear to be very important.

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[5] Using theoretical two-electron integrals and no interaction factors

Table 2 Contributions to and values of the INDO and NDDO one-center Fock matrix elements of N_2

INDO				
Element	F	U	$Z_B\gamma_{AB}$	G
s-s	-0.879102	-0.940096	-4.922956	4.983950
z-z	-0.215190	-0.486953	-4.922956	5.194719
s-z	-0.083180	0.000000	0.000000	-0.083180
x-x,y-y	-0.136620	0.486953	-4.922956	5.273289

NDDO				
Element	F	U	$Z_B(\mu\nu\|ss)$	G
s-s	-1.030826	-0.940096	-4.906097	4.815367
z-z	-0.387308	-0.486953	-5.114161	5.213806
s-z	-0.018901	0.000000	-0.600417	0.581516
x-x,y-y	-0.294039	-0.486953	-4.827421	5.020355

As to the balance in the Hamiltonian, the nuclear attraction integral contributions to the one-center Fock matrix are comparable, as one would expect for the two approximations. Relative to the averaged INDO values, the NDDO z-z element is slightly larger and the x-x and y-y elements, slightly smaller. However, the two-electron contributions have increased and decreased respectively, which compensates accordingly and maintains the crucial balance. Now, it may be that in larger molecules there is cumulative effect due to the sum over other centers which could lead to an unbalanced contribution. However, a similar examination of Fock matrix elements for benzene indicates that this is not the case. This conclusion is supported by the overall reasonable geometries obtained in the case of larger molecules in both methods.

Table 3. Contributions to and values of the INDO and NDDO two-center Fock matrix elements for N_2

INDO

Element	$F_{\mu\nu}$	$\beta_{\mu\nu}$	$G_{\mu\nu}$
ss	-0.469041	-0.410835	+0.058206
$\sigma\sigma$	+0.461225	+0.295723	-0.165502
$s\sigma$	-0.501348	0.403199	+0.098149
$\pi\pi$	-0.479978	-0.256270	+0.223708

NDDO

Element	$F_{\mu\nu}$	$\beta_{\mu\nu}$	$G_{\mu\nu}$
ss	-0.587544	-0.410835	+0.176709
$\sigma\sigma$	+0.564756	+0.295723	-0.269033
$s\sigma$	-0.609809	0.403199	+0.206610
$\pi\pi$	-0.488759	-0.256270	+0.232489

As can be seen from table 3, the INDO one-electron contribution to $F_{\mu\nu}$ has been maintained (as gvien by the Wolfsberg-Helmholz formula) in our NDDO model. Thus, the differences are entirely due to the inclusion of the NDDO integrals. In general the magnitude of each NDDO element is slightly greater than its corresponding INDO element.

Geometries

In this section are presented the results and some discussion of four different groups of calculations. Each group is comprised of a common set of molecules (chosen somewhat arbitrarily) but differ in the method used. Those labeled NDDO and NDDO/M were both carried out using the implementation of NDDO described previously but differ in the form chosen for the resonance integrals; the former using the WH type formula of Eq. (128) and the latter using the formulas due to Linderberg and Seamans discussed in the previous chapter. Corresponding sets of calculations were carried out at the INDO level for comparison and are labeled accordingly. Experimental results, where available, are also presented.

Diatomics

The NDDO bond lengths for the diatomic molecules listed in Table 4 are, with the exception of Li_2, slightly shorter than their INDO counterparts. Li_2 is slightly longer than its INDO counterpart but both the INDO and NDDO results are far enough from the observed value that the difference is hardly significant.

The NDDO/M and INDO/M results indicate that for homonuclear diatomics these methods will give generally shorter bond lengths compared to those obtained from NDDO and INDO. For the heteronuclear diatomics, CO and HF are slightly longer while LiH is slightly shorter.

Table 4 Calculated and observed equilibrium bond lengths (Å) for some diatomic molecules

Molecule	NDDO	NDDO/M	INDO	INDO/M	Obs. [92]
H_2	0.697846	0.644070	0.697646	0.643852	0.74172
Li_2	2.1650	1.8621	2.1490	1.8377	2.6725
N_2	1.1285	1.0801	1.1488	1.1035	1.094
O_2	1.1253	1.0689	1.1421	1.0908	1.20739
F_2	1.1027	1.0697	1.1140	1.0877	1.435
LiH	1.5313	1.4927	1.5314	1.4887	1.5953
HF	0.9693	0.9729	0.9781	0.9854	0.9171
CO	1.1778	1.2022	1.1953	1.2461	1.1281

Errors

RMS	0.1100	0.1618	0.1116	0.1650	N/A
AVG	0.0279	0.0437	0.0261	0.0409	N/A

Polyatomics

H_2O

Comparing the INDO and NDDO results for water, we see the now expected shortening (slight) of the O-H bond. An analysis of the Fock matrix elements similar to that discussed for N_2 indicates that this is more due to an increased nuclear-attraction term (residual penetration effect?) along the bonding axis than an effect of the NDDO two-electron integrals.

More interesting is the change in equilibrium bond angle from 102.6° to 112.13°. This I believe is a consequence of the NDDO type two-electron integrals. Of the coulombic integrals $\langle s_H s_O | s_H s_O \rangle$, $\langle s_H p_{z_O} | s_H p_{z_O} \rangle$ and $\langle s_H p_{y_O} | s_H p_{y_O} \rangle$, the smallest is the first which is the INDO γ_{AB}. Therefore it is reasonable to conclude that relative to NDDO, INDO will tend to underestimate the angular coulombic repulsions leading to generally smaller bond angles.

Table 5. Calculated and observed equilibrium bond lengths (A-B: Å) and angles (A-B-C: Degrees) for water

Bond/Angle	NDDO	NDDO/M	INDO	INDO/M	Obs. [93]
O-H	1.0018	0.9488	1.0193	0.9739	0.9571
H-O-H	112.13	130.7170	102.64	116.15	104.52

If we now look at the NDDO/M case we see that while the bond length is not unreasonable, the bond angle has increased to a point that is no longer acceptable. The cause now is a combined effect of the increased angular repulsions discussed above as well as a tendency for the LS formulas to yield a too large s-s interaction. This results in a lowest σ bonding with very little p character. By scaling $\beta_{s\text{-}s}$ by a factor of 0.75, additional p character is introduced into this molecular orbital reducing the bond angle (for the NDDO/M case) to a more acceptable 106° with a bond length of 1.102 Å. Scaling of the s-σ interaction by 1.3 introduces still more p character into the same molecular orbital and results in a more satisfactory bond length of 0.974 Å and bond angle of 102.5°.

HCN

The geometry of HCN is well reproduced. This is not easy to understand given that the equilibrium bond length for CO is calculated to large while that of N_2 is calculated to small.

Table 6. Calculated and observed equilibrium bond lengths for HCN

Bond	NDDO	NDDO/M	INDO	INDO/M	Obs. [93]
C-H	1.0619	1.0101	1.0752	1.0243	1.0632
C-N	1.1666	1.1273	1.1882	1.1493	1.1552

Ozone

Tables 7 and 8 give the optimized bond length and angle (in the C_{2v} case) for the C_{2v} and D_{3h} geometries of ozone. For C_{2v} ozone, as for water, there is a slight increase in equilibrium bond angle accompanied by a slight decrease in bond length on going from INDO to NDDO. This is consistent with previous observations and a similar analysis can be applied.

Table 7 Calculated and observed equilibrium bond lengths (A-B) and angles (A-B-C) for ozone (C_{2v})

Bond/Angle	NDDO	NDDO/M	INDO	INDO/M	Obs. [94]
O-O	1.1643	1.1057	1.1747	1.1206	1.278
O-O-O	122.46	136.24	120.34	132.79	116.49

The LS resonance integrals give an unacceptably large bond angle for both the INDO/M and NDDO/M cases. Unlike H_2O however, simply scaling the *s-s* interactions leads to only a moderate improvement reducing the angle by about 6° and increasing the bond length by 0.02 Å. Additional scaling of the *s-σ* interactions, also by 0.75, and the *σ-σ* interactions by 1.125 gives a bond angle of 114.21° and a bond length of 1.1812 Å. This is not inconsistent with the scaling used to improve the H_2O results and indicates that INDO/M and NDDO/M results might be significantly improved by a simple, uniform scaling of the LS resonance integrals.

Table 8 Calculated equilibrium bond length for ozone (D_{3h})

Bond	NDDO	NDDO/M	INDO	INDO/M
O-O	1.2415	1.1941	1.2470	1.2122

An important aspect of INDO calculations on ozone is the extent to which they incorrectly favor the closed-ring D_{3h} geometry over the experimentally observed

C_{2v} geometry. Table 9 gives the energies of the optimized D_{3h} and C_{2v} structures for each of the four methods examined in this work. A configuration interaction between the 4π and 6π-electron states that comprise the C_{2v} and D_{3h} structures lowers the C_{2v} state by 0.118 a.u. Thus the INDO/M and NDDO/M procedures are capable of correctly predicting the C_{2v} form lower in energy where the conventional INDO and NDDO methods are not.

Table 9: A comparison of the total energy of D_{3h} and C_{2v} ozone within the NDDO, NDDO/M, INDO, INDO/M methods

Geometry	NDDO	NDDO/M	INDO	INDO/M
D_{3h}	-51.241711	-50.472626	-50.455100	-49.636680
C_{2v}	-51.051192	-50.440249	-50.222322	-49.572490
Difference	0.190519	0.032377	0.232778	0.064190

Formaldehyde (H_2CO)

A generally observed feature of geometries obtained from ZDO methods is that the results tend to become more accurate as the size of the molecules increase. This effect is usually attributed to a fortuitous cancellation of errors as more and more terms contribute to the individual elements of the Fock matrix. In the formaldehyde results this trend begins to appear as the results for all four methods are quite reasonable.

Table 10 Calculated and observed formaldehyde equilibrium bond lengths (A-B) and angles (A-B-C)

Bond/Angle	NDDO	NDDO/M	INDO	INDO/M	Obs. [95]
C-O	1.2427	1.1963	1.2604	1.2140	1.2077
C-H	1.0808	1.0353	1.0945	1.0504	1.1159
H-C-H	118.29	113.54	118.23	112.15	116.50
H-C-O	120.86	123.23	120.88	123.92	121.75

Acetylene, Ethylene and Ethane

Tables 11, 12, and 13 give the calculated and observed geometries of acetylene (C_2H_2), ethylene (C_2H_4), and ethane (C_2H_6), respectively. These molecules provide familiar examples of saturated and unsaturated carbon-carbon bonds. Semi-empirical methods are often parameterized to match these experimental distances as closely as possible. The experimental range of bond distances in going from the carbon-carbon triple bond of acetylene to the carbon-carbon single bond of ethane is 0.3390 Å. This range is not well reproduced by any Hartree-Fock method, the problem being that the C-C bond length in ethane is predicted to be too short.

INDO/M gives a range for these bonds of 0.2799 or slightly longer than the 0.2774 predicted by INDO. The NDDO methods extend the calculated range by more than 0.01 Å to 0.2823 for NDDO/M and 0.2851 for NDDO. While this is only about 1% improvement, it is at least movement in the right direction. Overall, agreement among each of the methods with experiment is generally good. Comparing the methods among themselves show that the trend of NDDO/M < INDO/M < NDDO < INDO maintained for bond lengths and that all four methods reproduce the bond angles in these molecules rather well (all within less than 4° of experiment). Each of the methods correctly reproduces the increase in the C-H bond length from acetylene to ethane.

Table 11. Calculated and observed equilibrium bond lengths for acetylene

Bond	NDDO	NDDO/M	INDO	INDO/M	Obs [93]
C-C	1.1847	1.1683	1.2024	1.1904	1.2030
C-H	1.0609	1.0074	1.0751	1.0198	1.0598

Table 12. Calculated and observed equilibrium bond lengths (A-B) and angles (A-B-C) for ethylene

Bond/Angle	NDDO	NDDO/M	INDO	INDO/M	Obs. [93]
C-C	1.3116	1.3063	1.3233	1.3107	1.3390
C-H	1.0776	1.0263	1.0925	1.0452	1.0859
C-C-H	123.06	122.76	123.4	123.52	121.19
H-C-H	113.87	114.47	113.21	112.95	117.63

Table 13 Calculated and observed equilibrium bond lengths (A-B) and angles (A-B-C) for ethane

Bond/Angle	NDDO	NDDO/M	INDO	INDO/M	Obs. [96]
C-C	1.4698	1.4506	1.4798	1.4703	1.5429
C-H	1.0846	1.0415	1.0985	1.0570	1.1019
C-C-H	111.09	110.80	111.49	111.33	109.64
H-C-H	107.80	108.11	107.38	107.55	109.30

Borirane (C_2H_5B)

Although experimental evidence for the existence of borirane has been found [97–100], the molecule itself has not yet been isolated and characterized. Extensive *Ab initio* calculations [101] have determined that the small, non-planar ring form of C_2H_5B labeled (I) in Figure 6 is 0.0868 a.u. lower in energy than the planar structure (II) of the same figure.

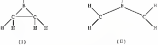

Figure 6 The closed-ring and planar open-ring structures of borirane

Semi-empirical INDO methods are notorious for overestimating the stability of small, closed-ring structures such as (I) relative to a corresponding open-ring structure (II). This is also the case with borirane. INDO calculations lead to the conclusion that the closed-ring structure (I) is 0.21 a.u. more stable than the open ring structure (I).

In order to determine whether or not NDDO or the use of LS resonance integrals (or a combination thereof) is capable of correcting this error in part or in whole, the closed and ring structures (I and II) of borirane where optimized using these methods. The results are presented in Table 14 and indicate that the tendency to favor small-ring formation is still quite strong. Furthermore, NDDO alone seems to intensify the problem rather than improve it relative to INDO. This is somewhat surprising since it might be expected that the anisotropic character of the NDDO two-electron integrals would tend to redistribute electronic repulsions in a more realistic fashion leading to better bond angles. in this case however, this is not observed.

Table 14. Calculated borirane energies (a.u.) for both the closed (I) and open (II) structures

Structure	NDDO	NDDO/M	INDO	INDO/M
I	-20.812118	-18.521706	-19.846130	-17.539277
II	-20.550769	-18.362983	-19.636571	-17.427151
Difference	-0.261349	-0.158723	-0.209559	-0.112126

There is some cause for optimism however, in that similar calculations utilizing the LS resonance integrals reduce the extent to which the closed ring form is favored by 0.097 a.u. for the INDO case and 0.103 a.u. for the NDDO case. It was also found that the optimal C-B-C bond angle is greatly overestimated in all cases and the problem is especially pronounced when using the LS resonance integrals. As discussed previously this problem can be partially corrected by scaling the s-s interactions thus infusing more *p* character into the σ bonding orbitals. One undesirable side effect of this scaling in the case of borirane is that the boron-hydrogen bond length is greatly increased (to 1.36 Å).

Such an effect indicates that a single atom-independent scale factor alone will not be sufficient for a systematic improvement of geometries using the LS resonance integrals. This of course implies introducing atomic parameters into the method. Another possibility is that the orbital exponents obtained from Slater's rules for INDO and used "as is" for NDDO and LS resonance integrals in this work may not be optimal.

Table 15 Calculated equilibrium bond lengths (A-B) and angles (A-B-C) for borirane with comparison to *ab initio* results.

Bond/Angle	NDDO	NDDO/M	INDO	INDO/M	*ab initio* [101]
B-C	1.5033	1.5759	1.5113	1.6139	1.54
C-C	1.5036	1.4573	1.5175	1.4728	1.56
B-H	1.1435	1.0923	1.1589	1.1047	1.17
C-H	1.0817	1.0323	1.0961	1.0459	1.08
C-B-C	60.014	55.079	60.269	54.295	60.6
H-C-H	109.42	112.38	110.31	113.79	112.8
C-B-H	149.99	152.46	149.87	152.85	149.7
B-C-H	120.72	117.44	120.47	115.72	120.1

Benzene and Pyridine

The geometries of benzene and pyridine were optimized with the results as shown in Tables 16 and 17. They are well reproduced.

Table 16 Calculated and observed equilibrium bond lengths for benzene[6]

Bond/Angle	NDDO	NDDO/M	INDO	INDO/M	Obs [93]
C-C	1.3806	1.3563	1.3942	1.3757	1.397
C-H	1.0798	1.0312	1.0959	1.0479	1.084

---

[6] All bond angles were constrained to the sp^2 hybrid angle of 120° for the optimization.

Table 17 Calculated and observed equilibrium bond lengths (A B) and angles (A B C) for pyridine

Bond/Angle	NDDO	NDDO/M	INDO	INDO/M	Obs [102]
N_1-C_6	1.3316	1.3078	1.3479	1.3390	1.342
C_6-C_5	1.3801	1.3665	1.3802	1.3757	1.391
C_5-C_4	1.3825	1.3810	1.3832	1.3786	1.398
C_4-H_9	1.0800	1.0482	1.0620	1.0488	1.075
C_3-H_8	1.0825	1.0622	1.1001	1.0575	1.080
C_2-H_7	1.0795	1.0282	1.0955	1.0498	1.085
$C_6N_1C_2$	120.31	117.96	118.07	119.50	116.42
$C_5C_4C_3$	119.93	117.76	118.43	121.43	118.60
$C_4C_3C_2$	118.29	118.55	119.44	117.39	118.36
$C_4C_3H_8$	122.35	125.33	120.81	125.10	121.70
$N_1C_2H_7$	115.88	117.70	114.89	116.61	115.44

Finally, the rms and average errors in the bond lengths and angles for each of the four methods over all of the molecules studied is presented in Table 18.

Table 18 Composite root mean square and average errors for bond lengths and angles over all of the molecules studied

	Bond Length Errors (Angstroms)			
	NDDO	NDDO/M	INDO	INDO/M
RMS	0.065	0.096	0.066	0.097
AVG	0.011	0.022	0.008	0.019

	Bond Angle Errors (Degrees)			
	NDDO	NDDO/M	INDO	INDO/M
RMS	1.657	4.890	1.119	3.316
AVG	-0.198	-0.771	0.036	0.350

Spectra

The success of the INDO/S method for the prediction of electronic spectra is well known. This being the case, it would seem that any other method which is to achieve widespread acceptance must perform at least as well. Furthermore, if the method is to impose additional overhead in terms of computing resources there must be enough of an improvement over INDO/S to justify this additional cost. However, if there is not a significant improvement in the results, the new method may still be justifiable on other grounds such as a more sound theoretical foundation or a lesser degree of parameterization. With the results that follow we hope to demonstrate that the methods we shall refer to as NDDO/S and NDDO/MS not only rest on a more sound theoretical foundation but also *could* be capable of greater accuracy than INDO/S.

Configuration Interaction

The calculation of electronic transitions is a two-step process. The first step is an MO-LCAO SCF calculation yielding molecular orbital coefficients and eigenvalues for the Hartee-Fock ground state. These calculations require as input an assumed geometry, atomic numbers and types of basis functions for each center, and the spin multiplicity. Geometries were taken either from experiment or the INDO optimized geometries when these were deemed reasonably close to the accepted experimental geometries. The basis set is inherently valence-only, minimal basis with orbital exponents from Slater's rules. Only ground state singlet molecules were studied.

The second step is a configuration interaction (CI) calculation in which pure configurations are generated by single excitations from the closed shell ground state into the unoccupied or *virtual* orbitals. If the ground state is represented by the determinant

$$\Psi_0 = |\psi_1\overline{\psi}_1 \cdots \psi_j\overline{\psi}_j \cdots \psi_N\overline{\psi}_N\rangle \tag{174}$$

then the excitation of an electron from the j-th occupied orbital to the a-th virtual orbital can take place in one of four possible ways yielding one of the four determinants

$$\Psi_j^a = |\psi_1\overline{\psi}_1 \cdots \psi_a\overline{\psi}_j \cdots \psi_N\overline{\psi}_N\rangle \tag{175a}$$

$${}^3\Psi_j^{\bar{a}} = |\psi_1\overline{\psi}_1 \cdots \overline{\psi}_a\overline{\psi}_j \cdots \psi_N\overline{\psi}_N\rangle \tag{175b}$$

$$ {}^3\Psi_j^a = |\psi_1\overline{\psi}_1 \cdots \psi_j\psi_a \cdots \psi_N\overline{\psi}_N\rangle \tag{175c} $$

$$ \Psi_{\bar{j}}^{\bar{a}} = |\psi_1\overline{\psi}_1 \cdots \psi_j\overline{\psi}_a \cdots \psi_N\overline{\psi}_N\rangle \tag{175d} $$

These are restricted open-shell determinants which, in general, are not eigenfunctions of $\mathbf{S}^2$, except when all the open-shell electrons have the same spin. However, by forming the appropriate linear combinations of those determinants which are not eigenfunctions of $\mathbf{S}^2$, new wavefunctions may be obtained which are eigen functions of $\mathbf{S}^2$. Such linear combinations are *spin adapted* configurations. For the case of the single excitation described above, the determinants ${}^3\Psi_j^a$ and ${}^3\Psi_{\bar{j}}^{\bar{a}}$ are pure triplets as indicated by the left superscripts. Using the remaining two determinants, we can form the spin adapted configurations

$$ {}^1\Psi_j^a = \frac{1}{\sqrt{2}}\left(\Psi_j^{\bar{a}} + \Psi_{\bar{j}}^{a}\right) \tag{176} $$

and

$$ {}^3\Psi_j^a = \frac{1}{\sqrt{2}}\left(\Psi_j^{\bar{a}} - \Psi_{\bar{j}}^{a}\right) \tag{177} $$

where the first is now a pure singlet and the second is a pure triplet. Considering only singlet-singlet transitions, the elements of the CI matrix are given by

$$ \langle\Psi_0|H|{}^1\Psi_j^a\rangle = 0 \tag{178} $$

in accordance with Brillouin's theorem and

$$ \langle{}^1\Psi_j^a|H - E_0|{}^1\Psi_k^b\rangle = (\varepsilon_a - \varepsilon_j)\delta_{jk}\delta_{ab} - (ak|bj) + 2(ak|jb) \tag{179} $$

Spectroscopic Parameterization

The results which follow are comparisons among four different methods, two at the INDO level and two at the NDDO level. The INDO/S results are well known but are included to serve as benchmark comparison for the INDO/MS, NDDO/S and NDDO/MS. All four methods are described briefly beginning with INDO/S since the others are most succinctly described in terms of how they differ from INDO/S.

INDO/S

The INDO/S method of Zerner and Ridley is well known for it accuracy in the prediction of the spectroscopy of large molecules. The essential elements of the INDO method have been described previously so only the details specific to the spectroscopic parameterization need be given and can be summarized as follows.

1. One-center, two-electron integrals γ_{AA}:

$$\gamma_{AA} = F_A^0(ss) = I_A - A_A \tag{180}$$

2. Two-center, two-electron integrals γ_{AB}:

$$\gamma_{AB} = \frac{f_\gamma}{\frac{2f_\gamma}{\gamma_{AA}+\gamma_{BB}} + R_{AB}} \tag{181}$$

$$f_\gamma = 1.2 \tag{182}$$

where the value 1.2 was chosen empirically to reproduce the naphthalene and anthracene spectra.

3 Two-center, one-electron integrals, $\beta_{\mu_A\nu_B}$:

$$\beta_{\mu_A\nu_B} = \frac{\beta_A^0 + \beta_B^0}{2} S_{\mu_A\nu_B} K_{\mu_A\nu_B} \qquad (183)$$

where S is the orbital overlap, the β^0's are chosen to give agreement with experiment and

$$K_{ss} = 1 \qquad (184a)$$

$$K_{sp} = 1 \qquad (184b)$$

$$K_{\sigma\sigma} = 1.267 \qquad (184c)$$

$$K_{\pi\pi} = 0.585 \qquad (184d)$$

INDO/MS

The INDO/MS method is very simply obtained from the INDO/S method by replacing the Wolfsberg Helmholtz formula for the two-center, one-electron core integrals with the equation of motion formulas due to Linderberg and Seamans as described in chapter 3. All other terms are as for INDO/S.

NDDO/S

The NDDO/S method is a spectroscopic modification of the NDDO method described in earlier in this chapter. This modification consists of replacing a spherically averaged piece of each purely coulombic two-electron integral with its Mataga-Nishimoto counterpart to obtain a new coulomb integral according to

$$\begin{aligned}(\mu_A\mu_A|\nu_B\nu_B)' &= [(\mu_A\mu_A|\nu_B\nu_B) - (\overline{\mu_A\mu_A|\nu_B\nu_B})]\kappa + \gamma_{AB} \\ (\mu_A\nu_A|\sigma_B\lambda_B)' &= [(\mu_A\nu_A|\sigma_B\lambda_B)]\kappa\end{aligned} \tag{185}$$

where κ is a scaling factor taken to be 0.6 where two-electron integral scaling is indicated and unity otherwise. The replacement of the averaged theoretical integral with its Mataga-Nishimoto equivalent is done in order to preserve the Mataga-Nishimoto functional form for coulomb integrals as required for the accurate calculation of π-π^* transitions. The scaling of the two-electron integrals is based on the observation that the theoretical integrals evaluated over the Slater basis are approximately 40% larger than the corresponding empirical Slater-Condon factors.

NDDO/MS

This method is the NDDO counterpart of INDO/MS, i.e., the Wolfsberg-Helmholtz resonance integral formula is replaced by the Linderberg-Seamans formulas.

Spectroscopic Results

Formaldehyde

Unsaturated molecules containing atoms such as nitrogen or oxygen, of which formaldehyde is a common example, often undergo forbidden n-π^* transitions. Since these are often the first (lowest energy) transitions observed in the ultraviolet spectrum they have been of great experimental and theoretical interest. These transitions are often poorly reproduced by INDO methods which seems to be a consequence of the two-electron scaling beneficial to the prediction of π-π^* transitions

The observed formaldehyde spectrum is shown in Table 19 and the calculated spectra in Tables 20 through 22. From these tables it is clear that the INDO/S method does not do a good job with formaldehyde and that the INDO/MS method is not an improvement. The NDDO/S and NDDO/MS methods without scaling of the two-electron integrals seems to reproduce well the first n-π^* transition but subsequent transitions are rather dramatically blue shifted. The NDDO/S method with scaled two-electron integrals seems to represent the worst of each extreme — the first transition being predicted too low and subsequent transitions much to high. The most interesting of all of the calculated formaldehyde spectra is the scaled two-electron NDDO/MS spectrum which is in the neighborhood of the INDO/S method for the first n-π^* transition but very accurate for the next two

Table 19: Observed formaldehyde spectrum

Observed [103]	
Type	Energy (cm^{-1})
$n-\pi^*$	28310
a	57014
a	64282
a	65573
a	71541

a) The assignment of these transitions is ambiguous as they seem to possess some Rydberg character.

Table 20: The INDO/S and INDO/MS spectrum of formaldehyde

INDO/S			INDO/MS		
Type	Energy (cm^{-1})	Oscillator Strength	Type	Energy (cm^{-1})	Oscillator Strength
$n-\pi^*$	25945	0.00	$n-\pi^*$	24828	0.00
$n-\sigma^*$	65250	0.03	$n-\pi^*$	50729	0.01
$\pi-\pi^*$	70979	0.33	$\pi-\pi^*$	56577	0.15
$n-\pi^*$	71584	0.02	$\sigma-\pi^*$	70221	0.00
$\pi-\sigma^*$	82896	0.03	$n-\sigma^*$	70309	0.04

Table 21. The NDDO/S and NDDO/MS (no scaling of the two-electron integrals) spectrum of formaldehyde

NDDO/S			NDDO/MS		
Type	Energy (cm^{-1})	Oscillator Strength	Type	Energy (cm^{-1})	Oscillator Strength
n-π^*	29123	0.00	n-π^*	28125	0.00
n-σ^*	85093	0.02	n-π^*	66589	0.01
π-π^*	86290	0.62	π-π^*	74979	0.42
n-σ^*	88090	0.08	σ-π^*	82488	0.00
σ-π^*	105089	0.00	n-σ^*	89815	0.19

Table 22. The NDDO/S and NDDO/MS (with scaling of the two-electron integrals) spectrum of formaldehyde

NDDO/S			NDDO/MS		
Type	Energy (cm^{-1})	Oscillator Strength	Type	Energy (cm^{-1})	Oscillator Strength
n-π^*	25367	0.00	n-π^*	24563	0.00
n-σ^*	76384	0.02	n-π^*	58087	0.01
π-π^*	77426	0.05	π-π^*	64916	0.24
n-π^*	78371	0.48	σ-π^*	80371	0.00
π-σ^*	96473	0.04	n-σ^*	81342	0.12

Benzene

The ultraviolet spectrum of benzene is well known and consists of two primary bands ($\nu_{max} = 55{,}900$ cm^{-1}, $\nu_{00} = 48{,}972$ cm^{-1}) and a secondary band at $\nu_{00} = 38{,}090$ cm^{-1}. All three of these bands correspond to π-π^* transitions. The second primary band is a dipole allowed transition ($A_{1g} \rightarrow E_{1u}$) polarized in the x,y planes and characterized by a large extinction coefficient (experimental oscillator strength of 0.690). The first primary band and secondary band correspond to dipole forbidden transitions ($A_{1g} \rightarrow B_{1u}$ and $A_{1g} \rightarrow B_{2u}$, repectively) and have small experimental oscillator strengths. The observed benzene spectrum is summarized in Table 23.

Table 23 Observed benzene spectrum

Observed [104]		
Type	Energy (cm^{-1})	Oscillator Strength
π-π^*	38090	0.001
π-π^*	48972	0.100
π-π^*	55900	0.690
σ-π^*	>60000	

The calculated INDO/S spectrum of benzene [36] (Table 24) is in good agreement with the observed spectrum as it should be having been parameterized specifically for benzene. Also in Table 24 are the INDO/MS results which give the first two π-π^* transitions as somewhat red-shifted compared to the INDO/S values The most notable feature of the INDO/MS results is the intrusion of a series of σ-π^* excited states between the first and second primary bands which is a result of the reordering of the degenerate σ mo's in the occupied space and the transposition of the highest π^* mo with a σ^* mo (relative to INDO/S) While this could be considered a serious flaw of the INDO/M method[7], it must be recalled that the model is parameter free. Thus considered, these results are not too bad and might be brought more in line with the INDO/S results by a simple scaling of the calculated LS resonance integrals.

Table 24 The INDO/S and INDO/MS spectrum of benzene

INDO/S			INDO/MS		
Type	Energy	Oscillator Strength	Type	Energy	Oscillator Strength
π-π^*	38875	0 0000	π-π^*	36930	0 0000
π-π^*	49163	0 0000	π-π^*	46190	0 0000
π-π^*	54743	1 0029	σ-π^*	50767	0.0000
π π^*	54743	1 0029	σ-π^*	51433	0 0000
π-π^*	58390	0 0000	σ-π^*	51433	0 0000
π-π^*	58390	0 0000	σ-π^*	52585	0 0029
σ-π^*	62396	0 0000	π-π^*	53889	1 0372
σ-π^*	62396	0 0000	π-π^*	53889	1 0372
σ-π^*	62616	0 0001	π-σ^*	62624	0 0000

---

[7] There is no experimental evidence for σ-π^* states below the allowed π-π^* band at 55,900 cm^{-1}

Tables 25 and 26 give the NDDO/S and NDDO/MS spectra of benzene without and with scaling of the two-electron integrals. The NDDO/S results are clearly flawed by the poorly positioned second π-π^* transition. This problem is corrected somewhat in the corresponding NDDO/MS spectrum but it is clear upon comparison with the Table 26 that the scaling of the two-electon integrals is necessary to reproduce the benzene spectrum.

The NDDO/MS spectrum of Table 26 is somewhat remarkable in that it represents a qualitatively accurate reproduction of the observed benzene spectrum using an essentially parameter-free semi-empirical model. Quantitatively, the spectrum is blue-shifted by approximatley 3,000 cm^{-1}.

Table 25 The NDDO/S and NDDO/MS (no two-electron integral scaling) spectrum of benzene

NDDO/S			NDDO/MS		
Type	Energy	Oscillator Strength	Type	Energy	Oscillator Strength
π-π^*	46138	0.0000	π-π^*	44370	0.0000
π-π^*	60191	0.0000	π-π^*	56948	0.0000
π-π^*	61848	1.3210	π-π^*	60481	1.2600
π-π^*	61848	1.3210	π-π^*	60481	1.2600
π-π^*	74863	0.0000	σ-π^*	70308	0.0000
π-π^*	74863	0.0000	π-π^*	71536	0.0000
σ-π^*	81600	0.0000	π-π^*	71536	0.0000
σ-π^*	81600	0.0000	σ-π^*	73072	0.0001
σ-π^*	81908	0.0043	π-π^*	73096	0.0000

Table 26 The NDDO/S and NDDO/MS (with two-electron integral scaling) spectrum of benzene

NDDO/S			NDDO/MS		
Type	Energy	Oscillator Strength	Type	Energy	Oscillator Strength
π-π^*	43265	0.0000	π-π^*	41429	0.0000
π-π^*	55550	0.0000	π-π^*	51748	0.0000
π-π^*	59331	1.2459	π-π^*	57426	1.1864
π-π^*	59331	1.2459	π-π^*	57426	1.1864
π-π^*	70947	0.0000	σ-π^*	63349	0.0000
π-π^*	70947	0.0000	σ-π^*	64823	0.0000
σ-π^*	74876	0.0000	σ-π^*	64823	0.0000
σ-π^*	74876	0.0000	σ-π^*	66722	0.0022
σ-π^*	75688	0.0012	π-π^*	68914	0.0000

Pyridine

The experimental pyridine spectrum is presented in Table 27. With the exception of the low-lying n-π^* transition due to the presence of the nitrogen lone pair, it is very similar to the benzene spectrum. The introduction of the nitrogen atom into the benzene ring is, in essence, a purturbation which breaks the D_{6h} symmetry, reducing it to C_{2v}. This perturbation is manifested in the calculated pyridine spectrum as a splitting of the degenerate E_{1u} state into two non-degenerate states of A_1 and B_2 symmetry.

The INDO/S pyridine spectrum of Table 28 gives generally good agreement with the observed spectrum. As was the case for benzene and β^0_C, the pyridine spectrum was the basis for the choice of β^0_N so this agreement is again not surprising. The INDO/MS spectrum (also in Table 28), on the other hand, does not correspond well with experiment and is rather dramatically red-shifted relative to the INDO/S spectrum. Furthermore the formerly degenerate E_{1u} transitions of benzene are now split by a σ-π^* transition which seems to indicate that the presence of nitrogen represents a larger perturbation of the benzene system in the INDO/MS model than one might expect.

Table 27 The observed spectrum of pyridine

Observed [105]		
Type	Energy (cm^{-1})	Oscillator Strength
n-π^*	34771	$\sim$0.003
π-π^*	38350	$\sim$0.040
π-π^*	49750	$\sim$0.10
π-π^*	$\sim$55000	$\sim$1.3
π-π^*	$\sim$56405	diffuse

Table 28 The INDO/S and INDO/MS spectrum of pyridine

INDO/S			INDO/MS		
Type	Energy	Oscillator Strength	Type	Energy	Oscillator Strength
n-π^*	35483	0.01	n-π^*	25789	0.00
π-π^*	38664	0.06	n-π^*	35729	0.00
n-π^*	43917	0.00	π-π^*	35730	0.03
π-π^*	49336	0.08	π-π^*	45763	0.01
π-π^*	55377	0.79	σ-π^*	49307	0.00
π-π^*	56067	0.89	n-π^*	51876	0.00
π-σ^*	57597	0.00	π-π^*	52928	0.84
n-π^*	61577	0.00	σ-π^*	54011	0.00
π-π^*	61939	0.01	π-π^*	54173	1.06

The results for pyridine using the NDDO/S and NDDO/MS models and unscaled two-electron integrals are presented in Table 29. While the NDDO/S spectrum gives the transitions in the same relative order as the INDO/S model the spectrum as a whole is blue-shifted from 6000 to 8000 cm^{-1} and the relative positions of the transitions are not well reproduced. An interesting aspect of the unscaled NDDO/MS spectrum is accuracy with which the first n-π^* transition is predicted. The remaining transitions are qualitatively correct but blue-shifted by approximately 4000 cm^{-1}.

Scaling the two-electron integrals red-shifts the NDDO/MS spectrum uniformly by approximately 3000 cm^{-1} relative to the unscaled calculation. The NDDO/S spectrum is also red-shifted relative to its unscaled counterpart but not as uniformly with shifts varying from about 2500 to 4000 cm^{-1}.

Table 29: The NDDO/S and NDDO/MS (no two-electron integral scaling) of Pyridine

NDDO/S			NDDO/MS		
Type	Energy	Oscillator Strength	Type	Energy	Oscillator Strength
$n-\pi^*$	42356	0.02	$n-\pi^*$	34550	0.01
$\pi-\pi^*$	44485	0.07	$\pi-\pi^*$	42331	0.06
$n-\pi^*$	52577	0.00	$n-\pi^*$	47138	0.00
$\pi-\pi^*$	58168	0.17	$\pi-\pi^*$	54728	0.01
$\pi-\pi^*$	61088	1.13	$\pi-\pi^*$	58658	1.07
$\pi-\pi^*$	62195	1.19	$\pi-\pi^*$	59614	1.31
$n-\pi^*$	71702	0.05	$n-\pi^*$	67252	0.00
$\pi-\pi^*$	72960	0.01	$\sigma-\pi^*$	68490	0.00
$n-\pi^*$	77124	0.00	$\pi-\pi^*$	70132	0.06

Table 30: The NDDO/S and NDDO/MS (with two-electron integral scaling) spectrum of Pyridine.

NDDO/S			NDDO/MS		
Type	Energy	Oscillator Strength	Type	Energy	Oscillator Strength
$n-\pi^*$	39668	0.02	$n-\pi^*$	31166	0.01
$\pi-\pi^*$	42057	0.03	$\pi-\pi^*$	39809	0.02
$n-\pi^*$	50893	0.00	$n-\pi^*$	44318	0.00
$\pi-\pi^*$	54197	0.14	$\pi-\pi^*$	50908	0.01
$\pi-\pi^*$	58516	1.15	$\pi-\pi^*$	55859	1.05
$\pi-\pi^*$	59808	1.13	$\pi-\pi^*$	56877	1.19
$\pi-\pi^*$	68028	0.02	$\sigma-\pi^*$	62733	0.00
$n-\pi^*$	70422	0.01	$n-\pi^*$	62931	0.00
$\pi-\pi^*$	72469	0.00	$\pi-\pi^*$	66390	0.02

Furan

The observed furan spectrum is given in Table 31. The calculated spectra appear in Tables 32 through 34. Many of the trends already noted among the four methods are again present. In this case however the first two observed bands are best reproduced by the NDDO/S and NDDO/MS methods, both without two-electron scaling. These methods however, predict subsequent bands, which are believed to possess some degree of Rydberg character, much too high. The corresponding scaled methods give better overall agreement with the observed spectrum although the first two transitions are red-shifted between 2 000 to 4 000 cm^{-1} from the observed values.

Table 31. The observed spectrum of furan

	Observed [106]	
Type	Energy (cm^{-1})	Oscillator Strength
	46512 - 51282	diffuse
	52219 - 57143	sharp bands
a	58824 - 63898	sharp bands
b	60790 64309	sharp

a) Possible Rydberg character; b) Rydberg character

Table 32 The INDO/S and INDO/MS spectrum of furan

INDO/S			INDO/MS		
Type	Energy	Oscillator Strength	Type	Energy	Oscillator Strength
π-π^*	42300	0.2456	π-π^*	39938	0 1814
π-π^*	46054	0 0055	π-π^*	43782	0 0006
π-σ^*	50171	0.0001	n-π^*	48423	0 0015
π-π^*	52305	0.0000	π-σ^*	53656	0.0000
π-π^*	60043	0.8219	π-σ^*	55404	0 0001
π-σ^*	63694	0 0590	n-π^*	57504	0.0000
π-π^*	64268	0 1135	σ-π^*	58300	0 0017
n-π^*	64393	0 0500	π π^*	60348	0.9799
π-σ^*	65074	0 0000	π-π^*	61288	0.0842

Table 33 The NDDO/S and NDDO/MS (no two-electron integral scaling) spectrum of furan

NDDO/S			NDDO/MS		
Type	Energy	Oscillator Strength	Type	Energy	Oscillator Strength
π-π^*	49663	0 3671	π-π^*	47798	0 3118
π-π^*	54241	0 0000	π-π^*	52409	0 0059
π-π^*	71085	1 2534	π-π^*	69289	1 1265
π-π^*	79855	0 1160	n-π^*	72059	0 0039
n π^*	83329	0.0003	π-σ^*	75077	0 0003
π-σ^*	83821	0.0000	π σ^*	75889	0 0000
π-σ^*	87084	0.0107	π-π^*	76655	0.0948
σ-π^*	91144	0 0000	σ-π^*	79769	0.0000
σ π^*	95214	0 0066	σ π^*	80043	0.0000

Table 34 The NDDO/S and NDDO/MS (with two-electron integral scaling) spectrum of furan

NDDO/S			NDDO/MS		
Type	Energy	Oscillator Strength	Type	Energy	Oscillator Strength
π-π^*	47101	0.3293	π-π^*	44688	0.2724
π-π^*	50546	0.0001	π-π^*	48281	0.0086
π-π^*	66027	1.1228	n-π^*	59658	0.0042
π-σ^*	69857	0.0016	π-π^*	63605	0.0130
σ-π^*	70469	0.0000	π-σ^*	65464	0.0020
π-π^*	71470	0.1442	π-π^*	67534	0.1304
n-π^*	73661	0.0095	π-σ^*	67856	0.0000
π-σ^*	81407	0.0000	σ-π^*	71326	0.0000
σ-π^*	83546	0.0000	σ-π^*	71796	0.0002

CHAPTER 5
CONCLUSIONS

The NDDO geometries reported here are only slightly better than those obtained from INDO while the INDO/M and NDDO/M geometries are not quite as good as their INDO counterparts These are in fact very positive results as INDO is a very highly refined method for which some effort has been expended in the determination of the optimal set of parameters. Such is not the case with the NDDO results reported here and I am confident that a systematic reparameterization of the NDDO method presented herein will yield geometries consistently superior to those obtained from INDO

As for INDO/M and NDDO/M, these are approximate methods in which the only parameters, save the orbital exponents are the atomic core parameters as determined from spectroscopy That the results are not only reasonable but quite good in some cases is remarkable. That they are not as good as the INDO and NDDO methods does not necessarily doom them to the graveyard of unsuccessful approximate methods. As is often the case in research, the stopping point of one project becomes the origin of several new ones and there are several aspects of the equation of method motion which warrant further investigation.

The first of the these is the choice of the functional form for $\beta_{\mu\nu}$ on which the remaining core Hamiltonian matrix elements (resonance integrals) depend. Linderberg and Seamans' choice has already been discussed (see Eq. 165 on page 70). Other choices are possible. For example, Zerner and Parr [107] suggested a Taylor's series expansion of β_{ss} according to

$$\beta_{ss} = \beta_{ss}^{0} + \beta_{ss}^{I}\lambda + \beta_{ss}^{II}\lambda^2 + \tag{186}$$

where

$$\lambda = \left(1 - \frac{R_c}{R}\right) \tag{187}$$

Since they were able to show that β_{ss}^{I} and β_{ss}^{II} can be approximated as constants times the appropriate orbital exponents, a one parameter (per atom pair) fit results from which they were able to reproduce force constants and anharmonic corrections for a wide assortment of diatomics.

Another possibility would be to maintain the Linderberg and Seamans choice for β_{ss} and treat the atomic transition moments as adjustable parameters. In some respects such a scheme would be preferable to that above in that it introduces no more parameters per atom (one for an s,p basis) than the Wolfsberg-Helmholz scheme. The rational being that no more parameters are introduced, the formulas are more soundly based in theory and, if the results are as good or better than those obtained from Wolfsberg-Helmholz, there is no loss of accuracy.

Also of interest, but not explored in this work, is a relation between the one center core Hamiltonian matrix elements which is a further result of the equation of motion method. This relation is

$$\kappa_A = u_A(U_{pp} - U_{ss}) \tag{188}$$

where κ is the one-center linear momentum integral. According to 188, the $U_{\mu\mu}$'s cannot be chosen independently. Since, these parameters come from atomic spectroscopy and are essential to a method which aspires to predict molecular spectra, changing them to satisfy this relationship is not recommended. However, given the spectroscopic $U_{\mu\mu}$'s, it is possible to evaluate Eq. (188) for the orbital exponents which might be more appropriate for use with this method. A preliminary investigation of this idea yielded, for carbon, an exponent of 1.29 (compared to 1.625), a value which is not outside the range of potential usefulness.

Common to both of the NDDO methods examined here is the neglect of penetration approximation implemented by setting V_{AB} equal to $Z_B\langle\mu_A s_B|\nu_A s_B\rangle$. The observed tendency of the NDDO two-center Fock matrix elements to be greater in magnitude than their INDO counterparts is consistent with the overall shorter bond lengths and blue-shifted spectra. Since the two-center core terms have already been addressed, the logical next point of attack could be the modification of $Z_B\langle\mu_A s_B|\nu_A s_B\rangle$ to $Z_B\langle\mu_A s_B|\nu_A s_B\rangle[f(R)]$ where $f(R)$ is some function of the distance between the charge distributions. This function could be parameterized if necessary.

It has no doubt occurred to the reader that this study has not touched upon the use of *d* orbitals and the obvious extension to transition metals. The prospects here are exciting and, for the most part, unexplored. Some work in this area has been done using the Linderberg-Seamans resonance integrals [108] but only at the INDO level with a highly parameterized spectroscopic Hamiltonian. The effect of the many more two-electron integrals at the NDDO level on the geometries and spectra of transition metal complexes is difficult to predict but certainly of great interest.

The prospect of a accurate, non-empirical, approximate method for molecular electronic structure may seem like a glimmer in the eye of so many hopeful theoreticians. However, such a method would be of enormous importance for the application of quantum mechanical methods to large and diverse molecular systems. It is my hope that this work is another step toward the formulation of such a method.

APPENDIX A
THE INDO METHOD

Zero Differential Overlap

The differential overlap of atomic orbitals on different atomic centers is neglected

$$S_{\mu_A \nu_B} = \delta_{\mu_A \nu_B} \tag{189}$$

Two-Electron Integrals

The ZDO approximation is again applied to the two-electron integrals such that

$$\langle \mu_A \sigma_C | \nu_B \lambda_D \rangle = \langle \mu_A \sigma_C | \nu_A \lambda_C \rangle \delta_{AB} \delta_{CD} \delta_{\mu\nu} \delta_{\sigma\lambda} \tag{190}$$

However, among the one and two-center integrals, all non-coulombic, two-center types are neglected while **all** one-center integrals are retained

$$\langle \mu_A \sigma_C | \nu_A \lambda_C \rangle = \left\{ \begin{array}{ll} \langle \mu_A \sigma_C | \mu_A \sigma_C \rangle \delta_{\mu\nu} \delta_{\sigma\lambda} & A \neq C \\ \langle \mu_A \sigma_A | \nu_A \lambda_A \rangle & A = C \end{array} \right\} \tag{191}$$

Since this approximation distinguishes between those two-electron integrals involving only one atomic center and those involving more than one atomic center it is expedient to express the summation over basis functions such that these different types are separated. Therefore, we rewrite it as

$$G_{\mu_A \nu_A} = A + B + C + D \tag{192}$$

with A, B, C, and D defined as follows

$$A = \sum_{C \neq A} \sum_{\lambda_C} \sum_{D \neq A} \sum_{\sigma_D} P_{\sigma_D \lambda_C} (\mu_A \lambda_C | \nu_A \sigma_D) - \frac{1}{2} \sum_{C \neq A} \sum_{\lambda_C} \sum_{D \neq A} \sum_{\sigma_D} P_{\sigma_D \lambda_C} (\mu_A \lambda_C | \sigma_D \nu_A) \tag{193}$$

$$B = \sum_{C \neq A} \sum_{\lambda_C} \sum_{\sigma_A} P_{\sigma_A \lambda_C} (\mu_A \lambda_C | \nu_A \sigma_A) - \frac{1}{2} \sum_{C \neq A} \sum_{\lambda_C} \sum_{\sigma_A} P_{\sigma_A \lambda_C} (\mu_A \lambda_C | \sigma_A \nu_A) \tag{194}$$

$$C = \sum_{\lambda_A} \sum_{D \neq A} \sum_{\sigma_D} P_{\sigma_A \lambda_D} (\mu_A \lambda_A | \nu_A \sigma_D) - \frac{1}{2} \sum_{\lambda_A} \sum_{D \neq A} \sum_{\sigma_D} P_{\sigma_A \lambda_D} (\mu_A \lambda_A | \sigma_D \nu_A) \tag{195}$$

$$D = \sum_{\lambda_A} \sum_{\sigma_A} P_{\sigma_A \lambda_A} (\mu_A \lambda_A | \nu_A \sigma_A) - \frac{1}{2} \sum_{\lambda_A} \sum_{\sigma_A} P_{\sigma_A \lambda_A} (\mu_A \lambda_A | \sigma_A \nu_A) \tag{196}$$

We can now apply the ZDO approximation within the INDO framework to the expression for the two-electron part of the Fock matrix. In doing so we note that both of the sums involving purely one-center terms are kept in accordance with Eq. (191). In the first summation on the right-hand side only terms of the form $(\mu_A \lambda_C | \mu_A \lambda_C)$ survive and in the third sum no terms survive since the summations include no orbitals on A, reducing the expression to

1 Case $\mu = \nu$, $A = B$

$$
\begin{aligned}
G_{\mu_A\mu_A} = & \sum_{C\neq A}\sum_{\lambda_C}\sum_{D\neq A}\sum_{\sigma_D} P_{\sigma_D\lambda_C}\langle\mu_A\lambda_C|\mu_A\sigma_D\rangle\delta_{CD}\delta_{\lambda\sigma} \\
& \underbrace{+\sum_{C\neq A}\sum_{\lambda_C}\sum_{\sigma_A} P_{\sigma_A\lambda_C}\langle\mu_A\lambda_C|\mu_A\sigma_A\rangle\delta_{AC}\delta_{\lambda\sigma}}_{0} \\
& \underbrace{+\sum_{\lambda_A}\sum_{D\neq A}\sum_{\sigma_D} P_{\sigma_A\lambda_D}\langle\mu_A\lambda_A|\mu_A\sigma_D\rangle\delta_{AD}\delta_{\lambda\sigma}}_{0} \\
& +\sum_{\lambda_A}\sum_{\sigma_A} P_{\sigma_A\lambda_A}\langle\mu_A\lambda_A|\mu_A\sigma_A\rangle \\
& \underbrace{-\frac{1}{2}\sum_{C\neq A}\sum_{\lambda_C}\sum_{D\neq A}\sum_{\sigma_D} P_{\sigma_D\lambda_C}\langle\mu_A\lambda_C|\sigma_D\mu_A\rangle\delta_{AD}\delta_{AC}}_{0} \\
& \underbrace{-\frac{1}{2}\sum_{C\neq A}\sum_{\lambda_C}\sum_{\sigma_A} P_{\sigma_A\lambda_C}\langle\mu_A\lambda_C|\sigma_A\mu_A\rangle\delta_{\mu\sigma}\delta_{\lambda\mu}\delta_{AC}}_{0} \\
& \underbrace{-\frac{1}{2}\sum_{\lambda_A}\sum_{D\neq A}\sum_{\sigma_D} P_{\sigma_A\lambda_D}\langle\mu_A\lambda_A|\sigma_D\mu_A\rangle\delta_{\mu\sigma}\delta_{\lambda\mu}\delta_{AD}}_{0} \\
& -\frac{1}{2}\sum_{\lambda_A}\sum_{\sigma_A} P_{\sigma_A\lambda_A}\langle\mu_A\lambda_A|\sigma_A\mu_A\rangle
\end{aligned}
\qquad (197)
$$

$$
\begin{aligned}
G_{\mu_A\mu_A} = & \sum_{C\neq A}\sum_{\lambda_C} P_{\lambda_C\lambda_C}\langle\mu_A\lambda_C|\mu_A\lambda_C\rangle \\
& +\sum_{\lambda_A}\sum_{\sigma_A} P_{\sigma_A\lambda_A}\left[\langle\mu_A\lambda_A|\mu_A\sigma_A\rangle - \frac{1}{2}\langle\mu_A\lambda_A|\sigma_A\mu_A\rangle\right]
\end{aligned}
\qquad (198)
$$

2 Case $\mu \neq \nu$, $A = B$:

$$
\begin{aligned}
G_{\mu_A\nu_A} = & \underbrace{\sum_{C\neq A}\sum_{\lambda_C}\sum_{D\neq A}\sum_{\sigma_D} P_{\sigma_D\lambda_C}\langle\mu_A\lambda_C|\nu_A\sigma_D\rangle\delta_{CD}\delta_{\mu\nu}\delta_{\lambda\sigma}}_{0} \\
& \underbrace{+\sum_{C\neq A}\sum_{\lambda_C}\sum_{\sigma_A} P_{\sigma_A\lambda_C}\langle\mu_A\lambda_C|\nu_A\sigma_A\rangle\delta_{AC}\delta_{\mu\nu}\delta_{\lambda\sigma}}_{0} \\
& \underbrace{+\sum_{\lambda_A}\sum_{D\neq A}\sum_{\sigma_D} P_{\sigma_A\lambda_D}\langle\mu_A\lambda_A|\nu_A\sigma_D\rangle\delta_{AD}\delta_{\mu\nu}\delta_{\lambda\sigma}}_{0} \\
& +\sum_{\lambda_A}\sum_{\sigma_A} P_{\sigma_A\lambda_A}\langle\mu_A\lambda_A|\nu_A\sigma_A\rangle \\
& \underbrace{-\frac{1}{2}\sum_{C\neq A}\sum_{\lambda_C}\sum_{D\neq A}\sum_{\sigma_D} P_{\sigma_D\lambda_C}\,\langle\mu_A\lambda_C|\sigma_D\nu_A\rangle\delta_{AD}\delta_{AC}\delta_{\mu\sigma}\delta_{\lambda\nu}}_{0} \\
& \underbrace{-\frac{1}{2}\sum_{C\neq A}\sum_{\lambda_C}\sum_{\sigma_A} P_{\sigma_A\lambda_C}\langle\mu_A\lambda_C|\sigma_A\nu_A\rangle\delta_{AC}\delta_{\mu\sigma}\delta_{\lambda\nu}}_{0} \\
& \underbrace{-\frac{1}{2}\sum_{\lambda_A}\sum_{D\neq A}\sum_{\sigma_D} P_{\sigma_A\lambda_D}\langle\mu_A\lambda_A|\sigma_D\nu_A\rangle\delta_{AD}\delta_{\mu\sigma}\delta_{\lambda\nu}}_{0} \\
& -\frac{1}{2}\sum_{\lambda_A}\sum_{\sigma_A} P_{\sigma_A\lambda_A}\,\langle\mu_A\lambda_A|\sigma_A\nu_A\rangle
\end{aligned}
\tag{199}
$$

$$
G_{\mu_A\nu_A} = \sum_{\lambda_A}\sum_{\sigma_A} P_{\sigma_A\lambda_A}\left[\langle\mu_A\lambda_A|\nu_A\sigma_A\rangle - \frac{1}{2}\langle\mu_A\lambda_A|\sigma_A\nu_A\rangle\right] \tag{200}
$$

3 Case $\mu \neq \nu$, $A \neq B$

$$G_{\mu_A\nu_B} = \underbrace{\sum_{C}\sum_{\lambda_C}\sum_{D}\sum_{\sigma_D} P_{\sigma_D\lambda_C}(\mu_A\lambda_C|\nu_B\sigma_D)\delta_{AB}\delta_{CD}\delta_{\mu\nu}\delta_{\lambda\sigma}}_{0}$$
$$-\frac{1}{2}\sum_{C}\sum_{\lambda_C}\sum_{D}\sum_{\sigma_D} P_{\sigma_D\lambda_C}(\mu_A\lambda_C|\sigma_D\nu_B)\delta_{AD}\delta_{BC}\delta_{\mu\sigma}\delta_{\nu\lambda} \tag{201}$$

$$\begin{aligned} G_{\mu_A\nu_B} &= -\frac{1}{2}\sum_{C}\sum_{\lambda_C}\sum_{D}\sum_{\sigma_D} P_{\sigma_D\lambda_C}(\mu_A\lambda_C|\sigma_D\nu_B)\delta_{AD}\delta_{BC}\delta_{\mu\sigma}\delta_{\nu\lambda} \\ &= -\frac{1}{2}\sum_{C}\sum_{D}\sum_{\sigma_D} P_{\sigma_D\nu_C}(\mu_A\nu_C|\sigma_D\nu_B)\delta_{AD}\delta_{BC}\delta_{\mu\sigma} \\ &= -\frac{1}{2}\sum_{D}\sum_{\sigma_D} P_{\sigma_D\nu_B}(\mu_A\nu_B|\sigma_D\nu_B)\delta_{AD}\delta_{\mu\sigma} \\ &= -\frac{1}{2}\sum_{D} P_{\mu_D\nu_B}(\mu_A\nu_B|\mu_D\nu_B)\delta_{AD} \\ &= -\frac{1}{2}P_{\mu_A\nu_B}(\mu_A\nu_B|\mu_A\nu_B) \end{aligned} \tag{202}$$

$$G_{\mu_A\nu_B} = -\frac{1}{2}P_{\mu_A\nu_B}\,(\mu_A\nu_B|\mu_A\nu_B) \tag{203}$$

We can now define $P_{CC} \equiv \sum_{\lambda_C} P_{\lambda_C\lambda_C}$ to arrive at

1 Case $\mu = \nu$, $A = B$

$$\begin{aligned} G_{\mu_A\mu_A} &= \sum_{C\neq A} P_{CC}(\mu_A\lambda_C|\mu_A\lambda_C) \\ &\quad + \sum_{\lambda_A}\sum_{\sigma_A} P_{\sigma_A\lambda_A}\left[(\mu_A\lambda_A|\mu_A\sigma_A) - \frac{1}{2}(\mu_A\lambda_A|\sigma_A\mu_A)\right] \end{aligned} \tag{204}$$

2. Case $\mu \neq \nu$, $A = B$

$$G_{\mu_A\nu_A} = \sum_{\lambda_A}\sum_{\sigma_A} P_{\sigma_A\lambda_A}\left[\langle\mu_A\lambda_A|\nu_A\sigma_A\rangle - \frac{1}{2}\langle\mu_A\lambda_A|\sigma_A\nu_A\rangle\right] \tag{205}$$

3. Case $\mu \neq \nu$; $A \neq B$

$$G_{\mu_A\nu_B} = -\frac{1}{2}P_{\mu_A\nu_B}\,\langle\mu_A\nu_B|\mu_A\nu_B\rangle \tag{206}$$

Rotational Invariance

To preserve rotational invariance in the two-electron integrals their values are assumed to be independent of the nature of the orbitals i.e.

$$\langle\mu_A\lambda_C|\mu_A\lambda_C\rangle = \gamma_{AC} \qquad \{A \neq C\} \tag{207}$$

1. Case $\mu = \nu$, $A = B$

$$\begin{aligned} G_{\mu_A\mu_A} = {} & \sum_{C\neq A} P_{CC}\gamma_{AC} \\ & + \sum_{\lambda_A}\sum_{\sigma_A} P_{\sigma_A\lambda_A}\left[\langle\mu_A\lambda_A|\mu_A\sigma_A\rangle - \frac{1}{2}\langle\mu_A\lambda_A|\sigma_A\mu_A\rangle\right] \end{aligned} \tag{208}$$

2. Case $\mu \neq \nu$, $A = B$

$$G_{\mu_A\nu_A} = \sum_{\lambda_A}\sum_{\sigma_A} P_{\sigma_A\lambda_A}\left[\langle\mu_A\lambda_A|\nu_A\sigma_A\rangle - \frac{1}{2}\langle\mu_A\lambda_A|\sigma_A\nu_A\rangle\right] \tag{209}$$

3 Case $\mu \neq \nu$, $A \neq B$.

$$G_{\mu_A \nu_B} = -\frac{1}{2} P_{\mu_A \nu_B} \gamma_{AB} \quad (210)$$

The Core Hamiltonian

The approximations for the core Hamiltonian potential terms are the same as those of the CNDO method (see chapter 2, section 2)

Resonance Integrals

The two-center core Hamiltonian matrix elements are given according to

$$H^{core}_{\mu_A \nu_B} = \langle \mu_A | -\frac{1}{2}\nabla^2 - V_A - V_B | \nu_B \rangle = \beta_{\mu_A \nu_B} \quad (211)$$

and are generally incorporated into the method as purely empirical parameters. The resulting equations are summarized at the end of chapter 2, section 3

APPENDIX B
THE NDDO METHOD

Zero Diatomic Differential Overlap

The differential overlap of atomic orbitals on different atomic centers is neglected.

$$S_{\mu_A \nu_B} = \delta_{\mu_A \nu_B} \tag{212}$$

Two-electron Integrals

The ZDO approximation is again applied to the two-electron integrals such that

$$\langle \mu_A \sigma_C | \nu_B \lambda_D \rangle = \langle \mu_A \sigma_C | \nu_A \lambda_C \rangle \delta_{AB} \delta_{CD} \tag{213}$$

In doing so, for the case of $\mu = \nu;\quad A = B$, the rhs of Eqs. (194) and (195) vanish as does the exchange piece on the rhs Eq. (193). Thus leaves

1. Case $\mu = \nu;\quad A = B$

$$\begin{aligned} G_{\mu_A \mu_A} = {} & \sum_{C \neq A} \sum_{\lambda_C} \sum_{\sigma_C} P_{\sigma_C \lambda_C} \langle \mu_A \lambda_C | \mu_A \sigma_C \rangle \\ & + \sum_{\lambda_A} \sum_{\sigma_A} P_{\sigma_A \lambda_A} \langle \mu_A \lambda_A | \mu_A \sigma_A \rangle \\ & - \frac{1}{2} \sum_{\lambda_A} \sum_{\sigma_A} P_{\sigma_A \lambda_A} \langle \mu_A \lambda_A | \sigma_A \mu_A \rangle \end{aligned} \tag{214}$$

For the case of $\mu \neq \nu$ $A = B$, the same terms vanish leaving the result as in the previous case with the obvious difference that μ and ν are no longer the same function.

2 Case $\mu \neq \nu$, $A = B$

$$\begin{aligned} G_{\mu_A \nu_A} = &\sum_{C \neq A} \sum_{\lambda_C} \sum_{\sigma_C} P_{\sigma_C \lambda_C} (\mu_A \lambda_C | \nu_A \sigma_C) \\ &+ \sum_{\lambda_A} \sum_{\sigma_A} P_{\sigma_A \lambda_A} (\mu_A \lambda_A | \nu_A \sigma_A) \\ &- \frac{1}{2} \sum_{\lambda_A} \sum_{\sigma_A} P_{\sigma_A \lambda_A} (\mu_A \lambda_A | \sigma_A \nu_A) \end{aligned} \tag{215}$$

3 Case $\mu \neq \nu$, $A \neq B$

$$\begin{aligned} G_{\mu_A \nu_B} = &\underbrace{\sum_{C} \sum_{\lambda_C} \sum_{D} \sum_{\sigma_D} P_{\sigma_D \lambda_C} (\mu_A \lambda_C | \nu_B \sigma_D) \delta_{AB} \delta_{CD}}_{0} \\ &- \frac{1}{2} \sum_{C} \sum_{\lambda_C} \sum_{D} \sum_{\sigma_D} P_{\sigma_D \lambda_C} (\mu_A \lambda_C | \sigma_D \nu_B) \delta_{AD} \delta_{BC} \end{aligned} \tag{216}$$

$$G_{\mu_A \nu_B} = -\frac{1}{2} \sum_{\sigma_A} \sum_{\lambda_B} P_{\sigma_A \lambda_B} (\mu_A \lambda_B | \sigma_A \nu_B) \tag{217}$$

The Core Hamiltonian

Two-center core Hamiltonian matrix elements are treated as empirical constants

$$H^{core}_{\mu_A \nu_B} = (\mu_A | -\frac{1}{2} \nabla^2 - V_A - V_B | \nu_B) = \beta_{\mu_A \nu_B} \tag{218}$$

APPENDIX C
SLATER-CONDON FACTORS

Two-Electron Integrals

Assuming a basis of the form

$$\varphi(r,\theta,\phi) = R_{nl}(r) Y_{lm}(\theta,\phi) \tag{219}$$

where $R_{nl}(r)$ is the radial part of the wave function and

$$Y_{lm}(\theta,\phi) \tag{220}$$

are the well known spherical harmonics, the general one-center, two-electron integral is

$$(is|jt) = \int\int\int \varphi_i^*(1)\varphi_s^*(2)\frac{1}{r_{12}}\varphi_j(1)\varphi_t(2)\,d\tau_1\tau_2 \tag{221}$$

or more explicitly

$$\begin{aligned}(is|jt) = \int_0^\infty \frac{1}{r_{12}} R^*_{n_i l_i}(1) R^*_{n_s l_s}(2) R_{n_j l_j}(1) R_{n_t l_t}(2) r_1^2 r_2^2\,dr_1\,dr_2 \\ \times \int_0^\pi\int_0^{2\pi} Y^*_{l_i m_{l_i}}(1) Y_{l_j m_{l_j}}(1) \sin\theta_1\,d\theta_1\,d\phi_1 \\ \times \int_0^\pi\int_0^{2\pi} Y^*_{l_s m_{l_s}}(2) Y_{l_t m_{l_t}}(2) \sin\theta_2\,d\theta_2\,d\phi_2\end{aligned} \tag{222}$$

The operator $\frac{1}{r_{12}}$ can be expressed in terms of an expansion over the spherical harmonics[8] as

$$\frac{1}{r_{12}} = \sum_{l=0}^{\infty} \sum_{m=-l}^{l} \frac{r_<^l}{r_>^{l+1}} P_l^{|m|}(\cos\theta_1) P_l^{|m|}(\cos\theta_2) e^{im(\phi_1-\phi_2)} \tag{223}$$

After substituting Eq. (223) into Eq. (222) and abbreviating the radial part of the integral as

$$R^k(is, jt) = \int_0^{\infty} R^*_{n_i l_i}(1) R^*_{n_s l_s}(2) \frac{r_<^k}{r_>^{k+1}} R_{n_j l_j}(1) R_{n_t l_t}(2) r_1^2 r_2^2 dr_1 dr_2 \tag{224}$$

we get

$$\begin{aligned} \langle is|jt \rangle = & \sum_{k=0}^{\infty} \sum_{m=-k}^{k} R^k(is, jt) \\ & \times \int_0^{\pi} \int_0^{2\pi} Y^*_{l_i m_{l_i}}(1) Y_{l_j m_{l_j}}(1) Y_{km}(1) \sin\theta_1 d\theta_1 d\phi_1 \\ & \times \int_0^{\pi} \int_0^{2\pi} Y^*_{l_s m_{l_s}}(2) Y_{l_t m_{l_t}}(2) Y_{km}(2) \sin\theta_2 d\theta_2 d\phi_2 \end{aligned} \tag{225}$$

Now, integration over the azimuthal angles yields a vanishing result unless the exponent is zero. This fixes the value of m according to

$$m = m_{l_i} - m_{l_j} = m_{l_t} - m_{l_s} \tag{226}$$

and reduces the summation over m to a single term. Furthermore, the integrals over the polar angle can be expressed in terms of the Clebsch-Gordon, or Wigner, coefficients [29] defined in the notation of Inglis and Shortley [11, 12] as

---

[8] See, for example, Jackson[109] page 102 or Slater [110] page 308

$$
\begin{aligned}
c^k(l_1 m_{l_1}, l_2 m_{l_2}) = {} & (-1)^{[m_{l_1}-|m_{l_1}|+m_{l_2}-|m_{l_2}|+m_{l_1}-m_{l_2}+|m_{l_1}-m_{l_2}|]/2} \\
& \times \sqrt{\frac{(k-|m_{l_1}-m_{l_2}|)!}{(k+|m_{l_1}-m_{l_2}|)!}} \times \sqrt{\frac{(2l_1+1)(l_1-|m_{l_1}|)!}{(l_1+|m_{l_1}|)!}} \\
& \times \sqrt{\frac{(2l_2+1)(l_2-|m_{l_2}|)!}{(l_2+|m_{l_2}|)!}} \\
& \times \frac{1}{2}\int_{-1}^{1} P_{l_1}^{|m_{l_1}|}(x) P_{l_2}^{|m_{l_2}|}(x) P_k^{|m_{l_1}-m_{l_2}|}(x)\, dx
\end{aligned}
\qquad (227)
$$

thereby simplifying the expression for the general two-electron integral to

$$
(is|jt) = \sum_{k=0}^{\infty} c^k(l_i m_{l_i}, l_j m_{l_j}) c^k(l_t m_{l_t}, l_s m_{l_s}) R^k(is, jt)\, \delta_{m_i+m_s,\, m_j+m_t} \qquad (228)
$$

If we now wish to take into account the orthogonality of the spin functions we simply multiply the term within the summation above by the factor $\delta_{m_{s_i}, m_{s_j}} \delta_{m_{s_s}, m_{s_t}}$ to arrive at a final expression. Before concluding this topic it is useful to consider two special cases–those of the Coulomb and exchange integrals

Coulomb Integrals

$$
\langle ij|ij\rangle = \sum_{k=0}^{\infty} c^k(l_i m_{l_i}, l_i m_{l_i}) c^k(l_j m_{l_j}, l_j m_{l_j}) R^k(ij, ij) \qquad (229)
$$

$$
a^k(l_i m_{l_i}, l_j m_{l_j}) = c^k(l_i m_{l_i}, l_i m_{l_i}) c^k(l_j m_{l_j}, l_j m_{l_j}) \qquad (230)
$$

$$F^k(n_i l_i; n_j l_j) = R^k(ij, ij) \qquad (231)$$

$$\langle ij|ij\rangle = \sum_{k=0}^{\infty} a^k(l_i m_{l_i}, l_j m_{l_j}) F^k(n_i l_i, n_j l_j) \qquad (232)$$

Exchange Integrals

$$\langle ij|ji\rangle = \sum_{k=0}^{\infty} c^k(l_i m_{l_i}, l_j m_{l_j}) c^k(l_i m_{l_i}, l_j m_{l_j}) R^k(ij, ji) \qquad (233)$$

$$b^k(l_i m_{l_i}, l_j m_{l_j}) = \left[c^k(l_i m_{l_i}, l_j m_{l_j})\right]^2 \qquad (234)$$

$$G^k(n_i l_i, n_j l_j) = R^k(ij, ji) \qquad (235)$$

$$\langle ij|ji\rangle = \sum_{k=0}^{\infty} b^k(l_i m_{l_i}, l_j m_{l_j}) G^k(n_i l_i, n_j l_j) \qquad (236)$$

An Example

Consider the 2p electrons of the determinant

$$|(100\alpha)(100\beta)(200\alpha)(200\beta)(211\alpha)(211\beta)\rangle \qquad (237)$$

of the configuration $(1s^2 2s^2 2p^2)$. This determinate has $M_L = 2$ and $M_S = 0$ and therefore must belong to the term ${}^1D$. The two-electron interactions of this single-determinant state can be written (ignoring the 2s electrons since their inclusion does little to enhance the illustration) as

$$\langle 2p_{(+1)} 2p_{(+1)} | 2p_{(+1)} 2p_{(+1)} \rangle \tag{238}$$

i.e. a single Coulomb integral with both electrons in a $2p$ $m_l = 1$ spatial orbital. According to the expressions above this integral simply evaluates to

$$\langle (211\alpha)(211\beta) | (211\alpha)(211\beta) \rangle = \sum_{k=0}^{\infty} a^k(11,11) F^k(21,21) \tag{239}$$

Now, although the sum over k is infinite, it turns out that there are only two values for which a^k is nonzero-zero and two. This leaves

$$\langle (211\alpha)(211\beta) | (211\alpha)(211\beta) \rangle = F^0(21,21) + \frac{1}{25} F^2(21,21) \tag{240}$$

Note that in this example, the actual spherical harmonics were assumed for the angular part of the function. In practice quantum chemists normally use the linear combinations of the spherical harmonics having the same l but opposite m_l values.

Considering now the exchange integral $\langle p_z p_x | p_x p_z \rangle$ where

$$\begin{aligned} p_z &= 2p_0 \\ p_x &= \frac{1}{\sqrt{2}} \left(2p_{(-1)} + 2p_{(+1)} \right) \end{aligned} \tag{241}$$

we have

$$\begin{aligned}\langle p_x p_z | p_x p_z \rangle = &\frac{1}{2}\langle 2p_{(-1)} 2p_0 | 2p_0 2p_{(-1)} \rangle \\ &+ \frac{1}{2}\langle 2p_{(-1)} 2p_0 | 2p_0 2p_{(+1)} \rangle \\ &+ \frac{1}{2}\langle 2p_{(+1)} 2p_0 | 2p_0 2p_{(-1)} \rangle \\ &+ \frac{1}{2}\langle 2p_{(+1)} 2p_0 | 2p_0 2p_{(+1)} \rangle\end{aligned} \tag{242}$$

which reduces to

$$\langle p_x p_z | p_x p_z \rangle = \frac{1}{2}\langle 2p_{(-1)} 2p_0 | 2p_0 2p_{(-1)} \rangle + \frac{1}{2}\langle 2p_{(+1)} 2p_0 | 2p_0 2p_{(+1)} \rangle \tag{243}$$

i e the second and third terms in the sum vanish due to the condition of Eq (226) It is now trivial to reduce the integral to a sum of Slater Condon factors to obtain

$$\begin{aligned}\langle p_x p_z | p_x p_z \rangle &= \frac{1}{2}\sum_{k=0}^{\infty}\left[\left[b^k(1,-1,1,0)\right]^2 + \left[b^k(1,1,1,0)\right]^2\right]G^k \\ &= \frac{1}{2}\left(\frac{3}{25}+\frac{3}{25}\right)G^2 \\ &= \frac{3}{25}G^2\end{aligned} \tag{244}$$

which of course is the same result obtained for the purely imaginary functions The only remaining detail is to show that $G^2 = F^2$ in this particular instance which is easy since the radial functions depend only on the principal and angular quantum numbers which are identical for the functions involved in the above integral Therefore we arrive at the final result of

$$\langle p_x p_z | p_x p_z \rangle = \frac{3}{25}F^2 \tag{245}$$

APPENDIX D
MISCELLANEOUS

Matrix Elements of [r,h]

Beginning with the definition of the commutator and the assumption of a complete basis set, we can make use of the resolution of the identity to obtain

$$\begin{aligned}\langle\mu_A|[\mathbf{r}\ h]|\nu_B\rangle = &\sum_C\sum_{\lambda_C}\langle\mu_A|\mathbf{r}|\lambda_C\rangle\langle\lambda_C|h|\nu_B\rangle \\ &-\sum_D\sum_{\lambda_D}\langle\mu_A|h|\lambda_D\rangle\langle\lambda_D|\mathbf{r}|\nu_B\rangle\end{aligned} \tag{246}$$

Using the assumption 2 of the development, namely that the matrix elements of the position operator are given by

$$\langle\mu_A|r|\nu_B\rangle = \delta_{AB}[\delta_{\mu\nu}R_A + \langle\mu_A|r - R_A|\nu_A\rangle] \tag{247}$$

and the one-center relative position operator matrix elements in an s, p basis are

$$\begin{aligned}\langle\mu_A|\mathbf{r}-\mathbf{R}_A|\nu_A\rangle = \mathbf{u}_A[&\mathbf{e}_x(\delta_{\mu s}\delta_{\nu x} + \delta_{\mu x}\delta_{\nu s})+ \\ &\mathbf{e}_y(\delta_{\mu s}\delta_{\nu y} + \delta_{\mu y}\delta_{\nu s})+ \\ &\mathbf{e}_z(\delta_{\mu s}\delta_{\nu z} + \delta_{\mu z}\delta_{\nu s})\,]\end{aligned} \tag{248}$$

or in matrix form

$$\langle\mu_A|\mathbf{r}-\mathbf{R}_A|\nu_A\rangle = \mathbf{u}_A\begin{bmatrix} 0 & \mathbf{e}_x & \mathbf{e}_y & \mathbf{e}_z \\ \mathbf{e}_x & 0 & 0 & 0 \\ \mathbf{e}_y & 0 & 0 & 0 \\ \mathbf{e}_z & 0 & 0 & 0 \end{bmatrix} \tag{249}$$

where u_A is an atomic transition moment integral. Then substituting Eq. (247) into Eq. (246) and performing the summation leaves

$$\begin{aligned}\langle \mu_A|\mathbf{r}h|\nu_B\rangle = \sum_{\lambda_A} \{ & \delta_{\mu_A\lambda_A}\mathbf{R}_A\langle\lambda_A|h|\nu_B\rangle \\ & + u_A[\mathbf{e}_x(\delta_{\mu_A s_A}\delta_{\lambda_A x_A} + \delta_{\mu_A x_A}\delta_{\lambda_A s_A}) \\ & + \quad \mathbf{e}_y(\delta_{\mu_A s_A}\delta_{\lambda_A y_A} + \delta_{\mu_A y_A}\delta_{\lambda_A s_A}) \\ & + \quad \mathbf{e}_z(\delta_{\mu_A s_A}\delta_{\lambda_A z_A} + \delta_{\mu_A z_A}\delta_{\lambda_A s_A})] \langle\lambda_A|h|\nu_B\rangle \}\end{aligned} \tag{250}$$

for the first term in the commutator and

$$\begin{aligned}\langle \mu_A|h\mathbf{r}|\nu_B\rangle = \sum_{\lambda_B} \{ & \delta_{\nu_B\lambda_B}\mathbf{R}_B\langle\mu_A|h|\lambda_B\rangle \\ & + u_B[\mathbf{e}_x(\delta_{\nu_B s_B}\delta_{\lambda_B x_B} + \delta_{\nu_B x_B}\delta_{\lambda_B s_B}) \\ & + \quad \mathbf{e}_y(\delta_{\nu_B s_B}\delta_{\lambda_B y_B} + \delta_{\nu_B y_B}\delta_{\lambda_B s_B}) \\ & + \quad \mathbf{e}_z(\delta_{\nu_B s_B}\delta_{\lambda_B z_B} + \delta_{\nu_B z_B}\delta_{\lambda_B s_B})]\langle\mu_A|h|\lambda_B\rangle \}\end{aligned} \tag{251}$$

for the second. Finally, summing over λ in Eqs. (250) and (251) gives

$$\begin{aligned}\langle \mu_A|\mathbf{r}h|\nu_B\rangle = & \mathbf{R}_A\langle\mu_A|h|\nu_B\rangle \\ & + u_A[\mathbf{e}_x(\delta_{\mu_A s_A}\langle x_A|h|\nu_B\rangle + \delta_{\mu_A x_A}\langle s_A|h|\nu_B\rangle) \\ & + \quad \mathbf{e}_y(\delta_{\mu_A s_A}\langle y_A|h|\nu_B\rangle + \delta_{\mu_A y_A}\langle s_A|h|\nu_B\rangle) \\ & + \quad \mathbf{e}_z(\delta_{\mu_A s_A}\langle z_A|h|\nu_B\rangle + \delta_{\mu_A z_A}\langle s_A|h|\nu_B\rangle)]\end{aligned} \tag{252}$$

$$\begin{aligned}\langle \mu_A|h\mathbf{r}|\nu_B\rangle = & \mathbf{R}_B\langle\mu_A|h|\nu_B\rangle \\ & + u_B[\mathbf{e}_x(\delta_{\nu_B s_B}\langle\mu_A|h|x_B\rangle + \delta_{\nu_B x_B}\langle\mu_A|h|s_B\rangle) \\ & + \quad \mathbf{e}_y(\delta_{\nu_B s_B}\langle\mu_A|h|y_B\rangle + \delta_{\nu_B y_B}\langle\mu_A|h|s_B\rangle) \\ & + \quad \mathbf{e}_z(\delta_{\nu_B s_B}\langle\mu_A|h|z_B\rangle + \delta_{\nu_B z_B}\langle\mu_A|h|s_B\rangle)]\end{aligned} \tag{253}$$

and gathering terms...

$$
\begin{aligned}
\langle\mu_A|[\mathbf{r}h]|\nu_B\rangle = (\mathbf{R}_A-\mathbf{R}_B)\langle\mu_A|h|\nu_B\rangle \\
+\quad \mathbf{e}_x\,[u_A(\delta_{\mu_A s_A}\langle x_A|h|\nu_B\rangle+\delta_{\mu_A x_A}\langle s_A|h|\nu_B\rangle) \\
-\quad u_B(\delta_{\nu_B s_B}\langle\mu_A|h|x_B\rangle+\delta_{\nu_B x_B}\langle\mu_A|h|s_B\rangle)\,] \\
+\quad \mathbf{e}_y\,[u_A(\delta_{\mu_A s_A}\langle y_A|h|\nu_B\rangle+\delta_{\mu_A y_A}\langle s_A|h|\nu_B\rangle) \\
-\quad u_B(\delta_{\nu_B s_B}\langle\mu_A|h|y_B\rangle+\delta_{\nu_B y_B}\langle\mu_A|h|s_B\rangle)\,] \\
+\quad \mathbf{e}_z\,[u_A(\delta_{\mu_A s_A}\langle z_A|h|\nu_B\rangle+\delta_{\mu_A z_A}\langle s_A|h|\nu_B\rangle) \\
-\quad u_B(\delta_{\nu_B s_B}\langle\mu_A|h|z_B\rangle+\delta_{\nu_B z_B}\langle\mu_A|h|s_B\rangle)\,]
\end{aligned}
\tag{254}
$$

Momentum Representation of Linear Momentum Matrix Elements

In coordinate space a two-center momentum operator matrix element is written as

$$
\begin{aligned}
\mathbf{p}_{\mu\nu} &= \int \phi_\mu^*(\mathbf{r})\mathbf{p}\phi_\nu(\mathbf{r}-\mathbf{R})d^3r \\
&= \int \phi_\mu^*(\mathbf{r})\frac{\hbar}{i}\nabla\phi_\nu(\mathbf{r}-\mathbf{R})d^3r
\end{aligned}
\tag{255}
$$

If we now change from coordinate to momentum space via the Fourier transformation

$$
\varphi_\mu(\mathbf{p}) = \left(\frac{1}{2\pi}\right)^{3/2}\int \phi_\mu(\mathbf{r})e^{-i\mathbf{p}\cdot\mathbf{r}}d^3r \equiv X_\mu(\mathbf{p}) \tag{256}
$$

and

$$
\varphi_\nu(\mathbf{p}) = \left(\frac{1}{2\pi}\right)^{3/2}\int \phi_\nu(\mathbf{r}-\mathbf{R})e^{-i\mathbf{p}\cdot(\mathbf{r}-\mathbf{R})}d^3r \equiv X_\nu(\mathbf{p})\,e^{i\mathbf{p}\cdot\mathbf{R}} \tag{257}
$$

the general momentum matrix element becomes

$$\mathbf{p}_{\mu\nu} = \int \mathbf{p} X_\mu(\mathbf{p}) X_\nu(\mathbf{p}) e^{i\mathbf{p}\cdot\mathbf{R}} d^3p \tag{258}$$

The plane wave $e^{i\mathbf{p}\cdot\mathbf{R}}$ can be expanded [113] as

$$e^{i\mathbf{p}\cdot\mathbf{R}} = \sum_{l=0}^{\infty} \sum_{m=-l}^{l} c_{l,m}\, j_l(pR)\, Y_l^m(\theta, \phi) \tag{259}$$

and in this case it is sufficient to specialize the expansion to

$$e^{i\mathbf{p}\cdot\mathbf{R}} = \sum_{l=0}^{\infty} a_l\, j_l(pR)\, P_l(\cos\theta) \tag{260}$$

θ being the angle between $\mathbf{p}$ and $\mathbf{R}$. Using the orthonormality of the Legendre polynomials we find that

$$a_l\, j_l(pR) = \frac{2l+1}{2} \int_{-1}^{+1} e^{ipR\cos\theta} P_l(\cos\theta) d\cos\theta \tag{261}$$

which can be compared with

$$j_l(pR) = \frac{1}{2i^l} \int_{-1}^{+1} e^{ipR\cos\theta} P_l(\cos\theta) d\cos\theta \tag{262}$$

to find

$$e^{ipR\cos\theta} = \sum_{l=0}^{\infty} (2l+1) i^l\, j_l(pR)\, P_l(\cos\theta) \tag{263}$$

Now, using this expansion in the expression for the gradient matrix element gives

$$\begin{aligned} \mathbf{p}_{\mu\nu} &= \int \mathbf{p}\, X_\mu(\mathbf{p}) X_\nu(\mathbf{p})\, e^{i\mathbf{p}\cdot\mathbf{R}}\, d^3p \\ &= \int \mathbf{p}\, X_\mu(\mathbf{p}) X_\nu(\mathbf{p}) \sum_{l=0}^{\infty} (2l+1) i^l\, j_l(pR)\, P_l(\cos\theta)\, d^3p \end{aligned} \tag{264}$$

which is useful for deriving relationships among the momentum matrix elements.

$$\nabla_{z\sigma} = \frac{d}{dR}(R\nabla_{x\pi}) \tag{265}$$

Beginning with the evaluation of the left hand side

$$\begin{aligned}\nabla_{z\sigma} &= \frac{1}{4\pi}\int X_{A_s}(p)\mathbf{p}\frac{1}{p^2}X_{B_z}(p)\cos\theta e^{i\mathbf{p}\cdot\mathbf{R}}d^3p \\ &= \frac{1}{4\pi}\int X_{A_s}(p)\Big(\underbrace{\sin\theta\cos\phi\,\vec{i}}_{1}+\underbrace{\sin\theta\sin\phi\,\vec{j}}_{2}+\underbrace{\cos\theta\,\vec{k}}_{3}\Big)\frac{|p|}{p^2}X_{B_z}(p)\cos\theta e^{i\mathbf{p}\cdot\mathbf{R}}d^3p\end{aligned} \tag{266}$$

Terms 1 and 2 vanish as can be seen by symmetry arguments considered earlier or by explicit integration over the azimuthal angle Considering now the third and only remaining term we have

$$\mathbf{p}_{z\sigma} = \nabla_{z\sigma}\mathbf{e}_z$$

$$\nabla_{z\sigma} = \frac{1}{4\pi}\int_0^\infty\int_0^\pi\int_0^{2\pi}\frac{|p|}{p^2}X_{A_s}(p)X_{B_z}(p)\cos^2\theta\, e^{i\mathbf{p}\cdot\mathbf{R}}p^2dp\sin\theta d\theta d\phi \tag{267}$$

and integration over the azimuthal angle gives

$$\nabla_{z\sigma} = \frac{1}{2}\int_0^\infty\int_0^\pi|p|X_{A_s}(p)X_{B_z}(p)\cos^2\theta\, e^{i\mathbf{p}\cdot\mathbf{R}}dp\sin\theta d\theta \tag{268}$$

Now, for the left-hand-side

$$\begin{aligned}\nabla_{x\pi} &= \frac{1}{4\pi}\int X_{A_s}(p)\frac{\mathbf{p}}{p^2}X_{B_x}(p)\sin\theta\cos\phi\, e^{i\mathbf{p}\cdot\mathbf{R}}d^3p \\ &= \frac{1}{4\pi}\int X_{A_s}(p)\frac{|p|}{p^2}\Big(\underbrace{\sin\theta\cos\phi\,\vec{i}}_{1}+\underbrace{\sin\theta\sin\phi\,\vec{j}}_{2}+\underbrace{\cos\theta\,\vec{k}}_{3}\Big)X_{B_x}(p)\sin\theta\cos\phi\, e^{i\mathbf{p}\cdot\mathbf{R}}d^3p\end{aligned} \tag{269}$$

Again after integration over the azimuthal angle, only the x-component survives so that

$$\mathbf{p}_{sx} = \nabla_{sx}\mathbf{e}_x \tag{270}$$

where

$$\begin{aligned}\nabla_{sx} &= \frac{i}{4\pi}\int_0^\infty\int_0^\pi\int_0^{2\pi} X_{A_s}(p)\frac{|p|}{p^2}X_{B_s}(p)\sin^2\theta\, e^{i\mathbf{p}\cdot\mathbf{R}}\cos^2\phi\, p^2 dp \sin\theta d\theta d\phi \\ &= \frac{i}{4}\int_0^\infty\int_0^\pi |p|X_{A_s}(p)X_{B_s}(p)\sin^2\theta\, e^{i\mathbf{p}\cdot\mathbf{R}}dp\sin\theta d\theta \end{aligned} \tag{271}$$

Since it is our intention to differentiate ∇_{sx} with respect to R, it is expedient to do so *before* expanding the plane wave to arrive at the final expression. However, we will first rewrite Eq. (271) as

$$\begin{aligned}\nabla_{sx} &= \frac{i}{4}\int_0^\infty\int_0^\pi |p|X_{A_s}(p)X_{B_s}(p)\sin^2\theta\, e^{i\mathbf{p}\cdot\mathbf{R}}dp\sin\theta d\theta \\ &= \frac{i}{4}\int_0^\infty\int_{-1}^{+1} |p|X_{A_s}(p)X_{B_s}(p)\left(1-\cos^2\theta\right) e^{ipR\cos\theta}dp\, d(\cos\theta) \\ &= \frac{i}{4}I\int_{-1}^{+1}\left(1-\cos^2\theta\right) e^{ipR\cos\theta}\, d(\cos\theta)\end{aligned} \tag{272}$$

where

$$I = \int_0^\infty |p|X_{A_s}(p)X_{B_s}(p)\, dp \tag{273}$$

Now, by the product rule

$$\frac{d}{dR}(R\nabla_{sx}) = R\frac{d}{dR}\nabla_{sx} + \nabla_{sx} \tag{274}$$

and

$$R\frac{d}{dR}\nabla_{sx} = \frac{1}{4}I\int_{-1}^{+1}(1-x^2)R\frac{d}{dR}\,e^{ipRx}\;dx$$

$$= \frac{1}{4}I\int_{-1}^{+1}(1-x^2)ipRx\;e^{ipRx}\;dx \tag{275}$$

where x has replaced $\cos\theta$ for brevity Now, substituting Eqs. (272) and (275) into (274) gives

$$\frac{d}{dR}(R\nabla_{sx}) = \frac{1}{4}I\int_{-1}^{+1}x(1-x^2)ipR\;e^{ipRx}\;dx + \frac{1}{4}I\int_{-1}^{+1}(1-x^2)\;e^{ipRx}\;dx \tag{276}$$

After integration by parts the first integral on the right-hand side of Eq (276) becomes

$$\frac{1}{4}I\int_{-1}^{+1}(3x^2-1)\;e^{ipRx}\;dx \tag{277}$$

Finally, combining the intermediate results gives

$$\frac{d}{dR}(R\nabla_{sx}) = \frac{1}{4}I\int_{-1}^{+1}(3x^2-1)\;e^{ipRx}\;dx + \frac{1}{4}I\int_{-1}^{+1}(1-x^2)\;e^{ipRx}\;dx$$

$$= \frac{1}{2}I\int_{-1}^{+1}x^2\;e^{ipRx}\;dx \tag{278}$$

which after replacing x with $\cos\theta$ and putting back in the definition of I leaves

$$\begin{aligned}\frac{d}{dR}(R\nabla_{sr}) &= \frac{1}{2}\int_{0}^{\infty} |p| X_{A_s}(p) X_{B_r}(p) \cos^2\theta \, e^{ipR\cos\theta} d(\cos\theta)\, dp \\ &= \frac{1}{2}\int_{0}^{\infty}\int_{0}^{\pi} |p| X_{A_s}(p) X_{B_r}(p) \cos^2\theta \, e^{i\mathbf{p}\cdot\mathbf{R}} \sin\theta d\theta dp\end{aligned} \tag{279}$$

Finally, comparison of the above with Eq (268) gives

$$\frac{d}{dR}(R\nabla_{sr}) = \nabla_{sr} \tag{280}$$

as we wished to show.

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BIOGRAPHICAL SKETCH

Charlie Taylor was born January 25, 1961, to Joan and Charles Taylor, Sr., in Jacksonville, Florida. Although he moved around a bit in his early years, he grew up, for the most part, in Valrico, Florida, where he attended Brooker Elementary School, Maddox Private School, Franklin Seventh Grade Center, McLane Junior High School and Brandon Senior High School.

Deciding that Florida summers were too hot and the landscape too flat, he left Valrico to attend Furman University in the foothills of the Blue Ridge. After obtaining his bachelor's degree in chemistry and deciding that winters in upstate South Carolina were too cold, he returned to Florida to attend graduate school at the University of Florida.

During his graduate school career he met, dated, and married Cindy Shelamer, lost two uncles, gained two brothers-in-law and two nephews, and saw his younger brother and sister through most of their high school and college years. He was witness to the Reagan revolution, the phenomenon of Music Television ("I want my mtv"), the Chernobyl nuclear catastrophe, the Challenger disaster, an uprising in Tiananman Square, and the fall of the Berlin Wall.

He firmly believes it is time to move on.

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy

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